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Treating Dinitrotoluene in Propellant Wastewater Using Anaerobic Fluidized-Bed Bioreactors Containing Granular Activated Carbon (GAC)

by
Stephen W. Maloney, Erica R. May, Makram T. Suidan, Sandra R. Berchtold, and Sarah Vanderloop

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This research was conducted for the U.S. Army Corps of Engineers (USACE), under Project 4A162720D048 Work Unit EP-T84, "Dinitrotoluene Abatement." The USACERL Principal Investigator was Dr. Stephen W. Maloney. The U.S. Army Environmental Center technical monitor was Richard Eichholtz, SFIM-AEC-TSD.

The study was performed by Dr. Makram T. Suidan, Sandra R. Berchtold, and Sarah L. Vanderloop of the University of Cincinnati, Cincinnati, OH and James G. Heffinger, Jr. and James E. Smith of Hercules Incorporated, Radford Army Ammunition Plant, Radford, VA, under contract to the Environmental Engineering Division (EP), Environmental Sustainment Laboratory (EL), U.S. Army Construction Engineering Research Laboratories (USACERL). Dr. Edgar D. Smith is Acting Chief, CECER-EP, and William Goran is Chief, CECER-EL.

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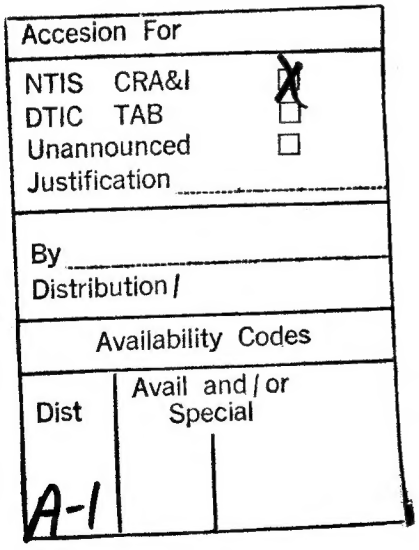

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1 Introduction

Background

The Environmental Protection Agency (EPA) has listed dinitrotoluene (DNT)* as a hazardous substance. Concern has arisen about the Army's use of the chemical in the manufacture of single-base propellants and trinitrotoluene (TNT) production because DNT is a suspected human carcinogen (Sweet 1992).

One of the biotransformed products of DNT is diaminotoluene (DAT), which is a proven cancer-causing agent in animals (U.S. Department of Health 1991, pp 146, 147). Because of the potential hazards these compounds contain, complete breakdown of both DNT and DAT is a high priority.

The U.S. Army Corps of Engineers (USACE) tasked the U.S. Army Construction Engineering Research Laboratories (USACERL) with determining possible treatments for DNT abatement. USACERL selected Radford Army Ammunition Plant (RAAP) in Radford, VA, for on-site research because the installation produces DNT-contaminated wastewater and cannot consistently meet the proposed National Pollution Discharge Elimination System (NPDES) permit peak DNT discharge limit of 285 micrograms/liter (µg/L) and monthly average discharge limit of 113 µg/L.

The main sources of DNT contamination at RAAP occur in the water-dry process and wet screening operation (PEI Associates 1991). In the water-dry process, various solvents, along with DNT, are leached from the propellant into a hot water bath (Maloney *et al.* 1992). The solvents, ethanol and ether, provide an easily biodegradable substrate that is often needed in co-metabolization of recalcitrant compounds like DNT.

Toxicity information on DAT is scarce, but all available information points to a higher toxicity than DNT (Appendix B). DAT was named as an effluent compound only midway through the research effort, when it was identified by chemists at RAAP and subsequently verified by the Hazardous Materials Laboratory/Hazardous Waste Research and Information Center (HML/HWRIC) in Champaign, IL and by the

*See Appendix A for the molecular structure of DNT.

chemistry laboratory at USACERL. As a result of this compound identification, analysis of DAT and its degradation by an aerobic mechanism were included in the research study.

Objectives

The objectives of this research were to determine a treatment that would reliably meet the EPA's regulatory limit. The research focused on the treatment of DNT under anaerobic conditions at the University of Cincinnati. The discovery of DAT during the study as the principal byproduct of anaerobic treatment led to the addition of another objective: to test the viability of breaking down the resulting DAT by aerobic processes.

Approach

A literature search was performed to gather information regarding past research in this and related areas. Next, the feasibility of biodegrading DNT under anaerobic conditions was evaluated under highly controlled laboratory conditions at the University of Cincinnati. Researchers used granular activated carbon (GAC) as an adsorbent and a surface for microbial attachment. The wastewater evaluated at the University of Cincinnati was modeled after the wastewaters at RAAP. The study was first conducted with only the anaerobic fluidized-bed bioreactors. After DAT was identified as the primary byproduct, two batch activated sludge reactors (aerobic systems) were added in series behind the two anaerobic columns at the University of Cincinnati to assess possible further degradation of this compound. The bench scale laboratory study at the University of Cincinnati continued while on-site research at RAAP commenced.

One of the bioreactors was shipped from the University of Cincinnati to RAAP to test actual wastewater instead of shipping the potentially hazardous wastewater to Cincinnati. The 400-mile trip also tested the ability of the active biomass to overcome stress and recover quickly, since the reactor was offline and without maintenance for 30 hours. This provided a way to estimate the stability of the system under variable feed concentrations and operational interruptions such as power outages.

Scope

The technology discussed in this report applies to biodegradation of specific nitroaromatics, and applies to those Army installations in the United States responsible for propellant production. Successful treatment of this hazardous compound by biodegradation will result in environmentally safe effluent constituents, which benefits not only the Army, but also the environment as a whole, while maintaining mission readiness.

Mode of Technology Transfer

Results of this evaluation have been transferred to the Army Environmental Center (AEC) for use in a demonstration at RAAP. Detailed cost estimates for scale-up will be developed after the demonstration.

2 Literature Review

PEI Associates (1991) evaluated several technologies for the treatment of DNT at RAAP, including GAC adsorption and UV/ozone oxidation. They recommended that both of these technologies be further studied on a bench scale. A brief summary of their results follow.

In PEI's evaluation of GAC adsorption, batch isotherm and flow-through column GAC tests evaluated the effectiveness of GAC for the removal of DNT from RAAP wastewaters. The results of these experiments were inconclusive because the adsorptive capacity estimated from the isotherm test was approximately 50% less than the adsorptive capacity derived from the flow-through column tests.

PEI's UV/ozone experiment succeeded in complete degradation of the DNT synthetic wastewater after 5 minutes of exposure. After this process was applied to actual water-dry water the UV/ozone showed a slower rate of destruction. However, this impeded rate was expected because of the presence of additional components which would have competed for the oxidation processes.

In reviewing the PEI report, USACERL researchers attributed the increase in capacity in the column test to biological activity observed on the carbon, which further implied possible biodegradation of DNT in the column adsorbers. Further work in this area was pursued immediately because of the discrepancy in the results of PEI's study. Because DNT is both adsorbable and biodegradable, it is a good candidate compound for treatment by combined adsorption and biodegradation. The GAC provides a buffer for variations in DNT concentration and variations in the ability of the attached biomass to degrade DNT.

The use of anaerobic fluidized beds for treatment of recalcitrant wastewaters has been under evaluation for over 15 years (Kahn *et al.* 1978). Conventional downflow adsorption was not considered for advanced study due to anticipated plugging by biomass, which will grow due to high ethanol concentration.

Biological processes have been used to treat wastewater for well over a century. Various reactor configurations have been developed and refined to deal with a variety of wastes. Generally, biological treatment processes can be divided into aerobic and

anaerobic processes. Aerobic processes require the presence of oxygen, while anaerobic processes require the absence of oxygen.

Aerobic processes are the most common and widely used wastewater treatment systems for the reduction of chemical oxygen demand (COD), although there has been an increase in the use of anaerobic processes over the past few years. A typical aerobic process used is activated sludge, which uses oxidation to convert organic wastes to carbon dioxide, water, ammonia, new cells, and other end products. (New cells may also be transformed to carbon dioxide, water, ammonia and energy through endogenous respiration.) However, there are several advantages that favor anaerobic treatment over aerobic treatment. In general, aerobic processes are easily started up, but produce more biomass than anaerobic processes. This biomass frequently requires costly disposal in landfills (as sludge). Anaerobic processes have a lower microbial yield (smaller amounts of biomass produced per amount of substrate consumed) compared to aerobic processes, and therefore generate lower quantities of sludge. Since anaerobic processes do not require additional oxygen for the system, further savings in energy costs can be realized (Metcalf and Eddy, Inc. 1991).

Of the various anaerobic processes, both methanogenesis and sulfate reduction have the potential for industrial waste treatment applications. Methanogenesis is attractive because a consortia of microorganisms (including methanogens) convert organic wastes through hydrolysis, acidogenesis, and methanogenesis to methane gas, a product that can be recovered and used as an energy source. Complete anaerobic biodegradation of DNT by methanogenesis will result in carbon dioxide, methane, and water, as well as traces of nitrogen gas and hydrogen sulfide gas, depending on the composition of the water supply used. This gas production is a good indicator of the general health of the microorganisms in the reactor, because the amount of gas can easily be measured.

Many anaerobic systems have been designed to recover methane. Nutrient requirements for methanogens include a number of heavy metals including cobalt, iron, molybdenum, nickel, magnesium and potassium. Methanogens also need ammonium ions to satisfy their nitrogen requirements. The need for sulfur varies among different methanogens, but is nonetheless required for growth. The optimum pH for methanogens varies within the neutral range of 6.6 to 7.6. They are inhibited at values below 6.2 (Metcalf and Eddy, Inc. 1991, p 425). They exhibit an ability to grow over a broad range of temperature (4 to 55 ^{o}C). The optimum temperature for most common strains is 35 °C. There is a strong temperature dependence, with an increase in activity from 10 °C to 37 °C that follows the Arrhenius equation.

Sulfate reducers use sulfate as an electron acceptor and an organic substrate to produce hydrogen sulfide (the infamous "rotten egg" smell). Hydrogen sulfide is chemically reactive and forms a black precipitate of compounds containing iron. It also can be toxic at concentrations of 0.2 parts per million (ppm).

For a long time, sulfate-reducing bacteria were thought to be a specialized group of organisms capable of degrading only a small number of organics like lactate and pyruvate. However, during the past few years a number of sulfate reducers have been isolated that are able to consume a variety of substrates including lactate, acetate, formate, propionate, higher straight and branched chain fatty acids, amino acids, sugars, and aromatic compounds. Nutrient requirements for sulfate reducers include magnesium, sodium, calcium and chloride. Sulfate reducers, like methanogens, use ammonium ions to satisfy their nitrogen requirements and also prefer a neutral environment for optimum growth. Most sulfate reducers are inhibited at pH values higher than 9 and lower than 6, but, like methanogens, can tolerate a large range of temperatures (from < 10 °C to 40 °C) (Metcalf and Eddy, Inc. 1991). Sulfate reducers were included in this research to work "side by side" with the methanogens in degrading DNT, in case the influent sulfate concentration of the wastewater had inhibitory levels of sulfate. Although methanogens do require sulfur as a nutrient, high amounts can be toxic to the system.

Because DNT is both adsorbable and biodegradable, both mechanisms are equally important in this study. The adsorption of DNT onto GAC can progress under aerobic and anoxic conditions. (Anoxic conditions are similar to anaerobic conditions in that they operate without the presence of oxygen, but unlike an anaerobic system, oxygen is not toxic to the microorganisms in an anoxic system.) After adsorption of DNT onto GAC, it was reported that under ambient conditions there were other compounds present besides DNT (Ho and Daw 1988). After analyzing solvent extracts of the carbon after the isotherm studies, six other compounds were detected, 2,4-dinitrobenzyl alcohol, 2,4-dinitrobenzaldehyde, 2,4-dinitrobenzoic acid, and 2,4-dinitrobenzoate and two unidentified compounds. The presence of these compounds on the GAC imply that oxidation occurs during or after the process of adsorption of DNT on the GAC. This may be due to the presence of oxygen as seen in other studies (Videc *et al.* 1990).

Although DNT and TNT are both biodegradable, there are only a few microorganisms that are known to perform this function. One hundred ninety species of fungi were screened and 183 were shown to be able to transform TNT, while only 5 were able to transform DNT (Parrish 1977). An isolated *Pseudomonas* species under oxidative pathways is able to utilize DNT as a sole carbon source (Spanggord *et al.* 1991). It was

reported that a co-substrate is needed as an energy source for the reactions under anaerobic conditions (Liu *et al.* 1984).

Once the biological reduction is underway, several different transformation paths can be taken. It was reported that TNT and DNT transformation under anaerobic conditions yielded nitrous and hydroxylamino intermediate compounds, which were then reduced to amino compounds as shown in the following reactions. Each reaction utilizes one mole of hydrogen.

$$R\text{-}NO_2 \text{ -----> } R\text{-}NO + H_2O$$
$$R\text{-}NO \text{ -----> } R\text{-}NHOH$$
$$R\text{-}NHOH \text{ -----> } R\text{-}NH_2 + H_2O \text{ (Liu } et\ al. \text{ 1984)}$$

It has also been reported that under anaerobic conditions, the nitro group in the *para* position was the most readily reduced, before the nitro group in the *ortho* position was transformed (McCormick *et al.* 1976). This observation suggests that the reaction is dependent on the position of the nitrate group. In a later study, it was concluded that DNT degraded into both 4-amino-2-nitrotoluene (4-A-2-NT) and 2-amino-4-nitrotoluene (2-A-4-NT), which implies that both the *ortho* and *para* nitro groups undergo the transformation, and that the position of the nitrate groups impacts very little on their transformation. This later study also identified four compounds and two dimers as degradation intermediates: 2-A-4-NT, 4-A-2-NT, DAT, 2,2'-dinitro-4,4'-azoxytoluene, 4,4'-dinitro-2,2'-azoxytoluene, and 4-acetamido-2-nitrotoluene (McCormick *et al.* 1978).

Fluidized-bed bioreactors have been demonstrated to be effective in treating toxic and inhibitory wastes such as coal gasification wastewaters and wastewaters containing chlorinated hydrocarbons (Suidan *et al.* 1983; Flora *et al.* 1993). Fluidized-bed reactors containing GAC combine the mechanisms of adsorption and biodegradation in treating wastewater. The GAC removes adsorbable compounds and provides a temporary storage location for adsorbable compounds that are difficult to degrade, thereby maintaining reactor stability to treat variable-strength wastewater and reduce shock load effects on the system. The GAC also serves as an excellent attachment media for microorganisms by providing a high specific surface area; this in combination with the turbulence within the reactor, allows a thin, dense biofilm to be grown easily, which results in a high biomass concentration within the reactor.

3 Methods and Materials

University of Cincinnati

Experimental Apparatus

Anaerobic bioreactors. At the University of Cincinnati, two identical fluidized-bed anaerobic columns were used during this study. These reactors were seeded with mixed liquor samples from the EPA Test and Evaluation Facility in Cincinnati. The reactors were operated in parallel using identical feed systems and piping networks. Figure 1* represents a schematic of these units. The 8-L column (10 L including recycle) consisted of an influent header, effluent header and jacketed tube. The inner jacketed tube (96.5 cm long, 10.2 cm inner diameter) was constructed from Plexiglas** and was enclosed by an outer Plexiglas tube. The recycle line was constructed from polyvinyl chloride tubing while the feed and effluent lines were constructed from Tygon and neoprene tubing. Water was circulated from a constant temperature bath (Model MW112CA Magna, Blue M Electric Co., Blue Island, IL) through the outer jacket, to maintain a constant temperature of 35 °C within the column. The effluent header was secured on the top of the jacketed portion to separate and convey the liquid effluent and off gas to respective effluent ports. Each column was charged with 1.0 kg of 16 x 20 U.S. Mesh F400 GAC (Calgon Corporation, Pittsburgh, PA).

The column was equipped with a side-arm (see Figure 1). The entrance to this side-arm was above the effluent header and the exit was below the recycle withdrawal port in the main column. The purpose of this side-arm was to allow the wetted virgin carbon to be added to the column without being caught in the recycle stream. It was also used to add the crushed solid DNT during operation.

The column was also equipped with a GAC withdrawal port located at the top of the effluent header. This allowed the GAC to be withdrawn from the column using a constant volume cup that could be placed at any desired level in the GAC bed to ensure a representative sampling of the GAC in the reactor.

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* Figures and tables are located at the end of each associated chapter.

** Plexiglas is a trademark of Rohm & Haas Co.

A recycle loop was used to maintain a constant bed expansion. This flow was maintained by a Model AC-3C-MD 3000 rpm centrifugal pump (March Manufacturing, Inc., Glenview, IL). A bed expansion of 30% was maintained throughout the study, which promoted gas-solid separation and prevented bed plugging. The influent header was filled with marbles to distribute the flow evenly through the column and to prevent attachment media from entering the recycle lines when the reactor was shut down.

Activated sludge reactors. Two identical aerobic activated sludge reactors were used during the batch part of this study. The primary components of the system were a 4-L aspirator bottle and a stone diffuser connected to a compressed air source. The activated sludge reactors were also seeded with mixed liquor samples collected from the activated sludge system operated at the EPA Test and Evaluation Facility. The effluent from the anaerobic GAC column was fed directly to the aerobic reactors. This provided the DAT to be biodegraded. A solution of nutrients was also added to supplement the anaerobic reactor effluent.

The continuous-flow activated sludge unit (which replaced one of the batch units) consisted of a 17.5 L Plexiglas tank (7.75 x 8.0 x 17.75 in. [19.685 x 20.32 x 45.085 cm]) with an upflow clarifier and a stainless steel diffuser 7 in. (17.78 cm) long and 0.25 in. (0.635 cm) in diameter (see Figure 2). A Plexiglas plate placed about 25 degrees from vertical provided means for clarification by being raised or lowered (manually) to adjust the width of the opening between it and the reactor wall. The biomass was brushed from the walls daily to decrease wall effects. The rate of aeration was stringently controlled to keep the system well mixed and to minimize any possible effects on sludge blanket quality due to aeration. This reactor was seeded with acclimated sludge from the batch-fed system and supplemented with mixed liquor samples from a local municipal wastewater treatment plant in Cincinnati.

Influent and effluent systems. Feed reservoirs for each column consisted of a 21-L glass aspirator bottle, containing the buffered and organic feed, and an 8-L glass aspirator bottle, containing a solution of salts and trace nutrients. A positive pressure head was maintained in each reservoir using a nitrogen blanket. A stainless steel syringe (35 mL capacity) was used to inject concentrated organic substrate using syringe pumps (Model 55-1111, pump 11, Harvard Apparatus, Inc., South Natick, MA). Stainless steel tubing was used for all syringe lines. The buffered and salt solutions were pumped to the recycle lines with a fixed-rpm pump drive (Masterflex Pump Model 7543-02 with Model 7015-20 pump head [buffer] and Model 7016-20 pump head [salts], Cole-Parmer Instruments Co., Chicago, IL). Bacterial growth in the feed reservoirs and the feed lines was prevented by pumping the salt solution into the recycle line at a point different from that used to feed the substrate solution. Bacterial

growth in the feed lines could cause inaccurate flowrate and clogging. Power to the Masterflex pumps was channeled through Dayton control timers. These on/off timers were used to adjust the flows and to obtain the proper hydraulic retention time.

Synthetic Feed Solutions

Nutrient solutions. The composition of the stock trace salt, salt, and vitamin solutions are presented in Tables 1, 2 and 3 respectively. The final nutrient solution was prepared by combining 30 mL of the stock vitamin solution (Table 3), 120 mL of the stock salt solution (Table 2; this also required the stock trace salt solution, found in Table 1), and diluting the solution with deionized water. (In the laboratory, 8-L containers were made at one time, which corresponds to 240 mL of the stock vitamin solution and 960 mL of the stock salt solution.) Ferrous chloride was also added (0.0833 g) with approximately 1.5 mL 37% hydrochloric acid. Addition of hydrochloric acid prevented the precipitation of iron. For the activated sludge reactors, 15 mL vitamin solution, 45 mL stock salt solution, and 0.0833 g ferrous chloride were added to the reactors every four days to supplement the influent feed. Ammonia was discontinued as feed to the continuous reactor when it was found the effluent ammonia from the anaerobic column and nitrate produced from the mineralization of DAT were sufficient for biological growth.

Buffer solutions. The buffer solutions were prepared according to the compositions given in Table 4. In addition to these compositions, each buffer solution contained sodium hydroxide concentrations, which were adjusted with every ethanol concentration change, to maintain a neutral pH. To supplement the organic feed from the syringe pumps, concentrations of ethanol and DNT were also added to the buffer reservoirs. The batch activated sludge reactors did not receive any buffer solution, whereas the continuous-flow reactor had a sodium carbonate and sodium hydroxide buffer system that maintained a pH of 8.0 in that unit (the optimum range for nitrifiers).

Syringe solution. Ethanol, petroleum ether, and DNT composed the syringe flow. This feed modeled synthetic wastewater (based on an evaluation of data collected from a water-dry process, which is the principle source of DNT) (PEI Associates 1991). Twenty-five mg DNT (97%, Aldrich Chemical Co., Milwaukee, WI) was dissolved in 1 mL of the ethanol/petroleum ether mix (0.94 mL 95% ethanol [Midwest Grain Products Co., Weston, MO.] and 0.06 mL petroleum ether [Aldrich Chemical Company, Inc., Milwaukee, WI]).

Data Collection

Anaerobic reactors. Both reactors were monitored daily by measuring total gas production, feed flow rates, reactor temperature, and reactor pH. Room temperature was also recorded to calculate methane production. Nutrient and substrate solutions were prepared as required without interrupting operation of the reactors.

Effluent liquid and gas samples were collected weekly to analyze for total and soluble COD, alcohols, volatile fatty acids, toluene, sulfate, DNT, and DAT. Liquid samples to be analyzed were filtered through 0.45 µm Magna nylon filters and acidified to a pH of 2 with phosphoric acid. Samples were then stored at 5°C. Effluent gas samples were analyzed for gas composition.

GAC samples were taken from the fluidized bed throughout the experiment and analyzed for adsorbed DNT and its degradation products.

COD balances were updated regularly on a Lotus 1-2-3* spreadsheet. The balances were used to calculate how much COD was converted to methane and how much COD was retained in the reactor. Percent conversion of COD to methane was based on the COD due to ethanol, petroleum ether, and DNT in the feed. The COD balances signified how well the system was performing and whether the results from analysis were logical.

Activated sludge reactors. The batch activated sludge reactors were analyzed daily for influent and effluent concentrations of DNT, DAT, 2-A-4-NT, and 4-A-2-NT. The influent, effluent, and settled sludge volumes were also measured daily. Samples were pulled twice a week from the continuous reactor and analyzed for ammonia and nitrate in order to calculate a nitrogen balance around the reactor.

Analytical Methods

Ammonia and nitrate. The ammonia concentration was measured with a model 720A Orion pH meter (Orion Research Co., Boston, MA) using a Model 13-620-505 ammonia ion selective electrode (Fisher Scientific, Pittsburgh, PA) and an Orion Model 215284-AO1 ATC probe. A Model 9307BN Orion nitrate electrode and Model 90002000 Orion reference electrode were used to measure nitrate concentration.

pH. Reactor pH was analyzed immediately following withdrawal of the liquid sample, to prevent any change in the pH due to the release of CO_2. A Model 720A Orion pH

* Lotus 1-2-3 is a trademark of Lotus Development Corp.

meter (Orion Research Co., Boston, MA) with combination probe Model 13-620-288 (Fisher Scientific, Pittsburgh, PA), was used to measure the pH. To accurately determine the pH, the meter was calibrated with buffers at 7 and 4.

Gas composition. Effluent gas samples from the reactors were analyzed for nitrogen, oxygen, carbon dioxide, and methane with a Model 900 Perkin Elmer Gas Partitioner. The gas partitioner was calibrated with certified gas standards (Matheson Gases and Equipment, Pittsburgh, PA).

Total methane production per day was calculated by combining the methane content, total gas production, gas pressure, and gas temperature. Methane production was corrected for water vapor, and Henry's Law was used to estimate the volume of dissolved methane in the liquid effluent.

Chemical oxygen demand. Samples were analyzed for COD (American Public Health Assoc. 1985, pp 537, 538). Filtered samples were acidified with 85% *o*-phosphoric acid to a pH of 2 and purged with prepurified nitrogen for 10 minutes to strip out the sulfide. Prepared Hach COD glass vials (range 0 - 150 mg/L) and Hach COD reactor Model 45600 (Hach Co., Loveland, CO) were used for the analysis. The percent transmittance of the digested samples was read using a Bausch and Lomb Spectronic 70 spectrophotometer.

Volatile fatty acids. Aqueous injection in a gas chromatograph (GC) was used to analyze for volatile fatty acids. GC conditions for this analysis can be found in Table 5. Calibration was for acetic and propionic acid, with butyric acid as an internal standard (0.03 molar [M] oxalic acid was added to each standard and sample). The detection limits for acetic acid and propionic acid were 0.1 and 0.05 mg/L, respectively. The ratio of sample to internal standard was 5 to 1.

Alcohols. Alcohol analysis was also accomplished by GC. The conditions can be found in Table 6. Calibration was for methanol and ethanol, with propanol as the internal standard. The detection limits for methanol and ethanol were 0.1 and 0.1 mg/L, respectively. The ratio of sample to internal standard was 5 to 1.

GAC adsorption isotherms. Isotherms were established on 16 x 20 U.S. Mesh F400 Calgon GAC (the same carbon used throughout the experiment). Conditions in the anaerobic reactor were simulated by evaluating the isotherms under oxic and anoxic conditions at 35°C.

For oxic conditions, a known weight of GAC was added to 100 mL of 40 mg/L and 110 mg/L DNT buffered solutions in 160-mL serum bottles. The head space was then

purged with oxygen and subsequently sealed and crimped. Anoxic conditions were obtained by purging with nitrogen the buffered water used to make the DNT solutions. DNT was added to the buffered water under a nitrogen blanket. The serum bottles were again purged with nitrogen to remove air from the head space before they were completely filled and sealed. Two-thirds of the serum bottles were shaken for 14 days before analysis was performed. The remaining third were shaken for an additional 7 days (a total of 21 days) to ensure that equilibrium was attained. The lack of significant differences between the samples analyzed after 14 and 21 days indicated that equilibrium had been obtained.

Extraction of GAC. GAC samples were removed from a reactor and extracted to quantitatively analyze the compounds adsorbed on the GAC. A known weight of GAC was extracted with methanol in a soxhlet extraction apparatus for a period of one day, and then with methylene chloride for three days. The methanol was used to help eliminate water from the pores of the GAC. The GAC extractions were measured via GC, and the extracted GAC was dried and weighed.

DNT and degradation products. An aqueous sample was raised to a pH of 12 with 10M sodium hydroxide and extracted with ether in a 5 to 1 ratio of sample to ether. (DNT was not affected by this pH during the GC analysis.) Quinoline, the internal standard, was contained in the ether. The ether extract was then used in the GC. Conditions for this analysis are located in Table 7. Effluent samples of both columns and of the activated sludge reactors were analyzed for both DNT and DAT. Detection limits for DAT, 2-A-4-NT, 4-A-2-NT, and DNT were 0.3, 0.1, 0.1, and 0.03 mg/L, respectively.

Carbon extraction from both reactor samples and isotherm carbon were contained in methanol with a quinoline internal standard. Using the same temperature program as ether, the extractions were analyzed for DNT in isotherm extractions and DNT, DAT, 2-A-NT, and 4-A-2-NT in reactor carbon extractions.

Toluene. A 5-mL sample of effluent filtered in-line was injected into a Tekmar LSC-2 purge and trap. The sample was purged for 12 minutes with helium. The gas phase entered a column in a Hewlett Packard 5890 GC equipped with a Hewlett Packard photo ionization detector. The temperature program for the GC was $40^{o}C$ for 4 minutes and then ramped $5^{o}C$ per minute to $120^{o}C$. The detection limit for toluene was 0.1 µg/L.

Sulfate. Sulfate analysis was performed on Column B while it was receiving sulfate through the buffer (American Public Health Assoc. 1985, p 466). The method involved precipitating the sulfate with barium chloride. The resulting barium sulfate

precipitate was then filtered and weighed using a Shimadzu Libror AEL-40SM electronic analytical balance (Shimadzu Corp., Kyoto, Japan). The difference between the influent and effluent sulfate to the reactor was used to calculate the amount of COD degraded via sulfate reduction.

Radford Army Ammunition Plant

There were two phases to this project while at RAAP. Phase I, a two-month time period, was used to evaluate the reactor for the removal and destruction of DNT from RAAP process wastewater at the same flow rate used at the University of Cincinnati (approximately 5 L/day), and to provide data to assess this laboratory process for large-scale application. Phase II lasted three months and was originally planned to study the effects of increasing influent flow rates on the column. Although there were problems with the increase in flow rates, there were still only three days in which the effluent levels of DNT were above 3 mg/L.

Experimental Apparatus

The entire system used at RAAP (column, water bath, gas tip meter, pumps, timers) was very similar to the reactor used at the University of Cincinnati. However, the reactor at RAAP did not have the side-arm attached to it for additional DNT feed, since this was not required. A process flow diagram of the GAC anaerobic reactor used at RAAP is presented in Figure 3. The main components of the fluidized-bed bioreactor consisted of a column with a water jacket, dual feed systems for vitamin/salt and buffer/feed solutions, recycle loop, and a gas meter. A recirculating water bath was again used to maintain the temperature of the GAC column at 35°C by providing heated water to the water jacket of the column. A recycle loop was used to fluidize the GAC with biomass attached in the column, as well as feed the vitamin/salt solution and buffered solutions. The gas generated passed through a sodium hydroxide solution to remove carbon dioxide and other soluble gases, so all of the gas measured was assumed to be methane. The biogas generated during biodegradation was then vented from the top of the column and measured by a gas meter. The custom gas meter was developed by and purchased from Dr. Richard Speece, currently Chair of Environmental Engineering at Vanderbilt University.

A hazards analysis evaluation of the equipment and operations (see Appendix C) was performed by Hercules; they determined that no unacceptable risks were present for pilot-scale testing.

Feed Solution

Because the GAC anaerobic reactor arrived at RAAP already acclimated to 600 mg/L ethanol and 40 mg/L DNT, true wastewater was initiated on Day 2 at a flow rate of 6 L/day. Buffers, trace salts and vitamins were fed to favor methanogens. The same setup was used to deliver the buffered and nutrient solutions to this system as had been used at the University of Cincinnati. Nutrient solutions were prepared by University of Cincinnati personnel and shipped to RAAP.

Data Collection

Measurements were taken that recorded the buffer, nutrient, and DNT wastewater flowrates, pH, gas production, and water bath temperature on a daily basis for Phase I and generally twice a week for Phase II. High-performance liquid chromatographic (HPLC) analysis for DNT was performed on the influent and effluent at regular intervals. Volatile acids, alcohol, gas composition, COD, and DNT (Cold Regions Research and Engineering Laboratory [CRREL] method [Miyares and Jenkins 1991]) analyses were also performed at regular intervals. The CRREL technique was used to concentrate the sample to improve the detection limits for DNT and DNT-related biodegradation by-products (in this case, DAT). Additionally, the University of Cincinnati provided support and analysis of various samples throughout the evaluation.

Analytical Methods

DNT and metabolite analysis. Samples of reactor influent and effluent were collected for DNT analysis. The influent samples were not pH adjusted; however, the effluent samples were adjusted to a pH of 2 with phosphoric acid. They were analyzed on the same day for DNT by the routine laboratory HPLC method. The specifics of the method are outlined in Table 8 .

One-quart samples of the reactor effluent were collected for the analysis of DNT and its metabolites by two analytical methods. These samples were stored at 4°C and were not pH adjusted.

DNT was analyzed using two methods, due to the wide range in concentration. The high-range method uses direct liquid chromatography as practiced for process monitoring at RAAP. Low-level analysis of DNT was performed using an extraction concentration technique developed by CRREL. This latter technique is capable of determining concentrations of less than 1 µg/L.

In the first method, the sample was acclimated to room temperature, then an aliquot was filtered through a 0.45-µm Millex filter. The sample was analyzed for DAT by the HPLC method specified in Table 9 (using RAAP procedure LTA-7). This method will be referred to as the "RAAP method."

In the second method, the sample was allowed to acclimate to room temperature, then a 400-mL aliquot was removed for extraction. The sample was placed in a 500-mL separatory funnel, and 130 grams of sodium chloride were added. The sample was shaken until all of the salt was dissolved, and the pH was adjusted to approximately 12 with a 20% sodium hydroxide solution. One hundred mL of acetonitrile were added and the sample was shaken with frequent venting. The acetonitrile layer was drawn off into a 100-mL Griffin beaker, and an additional 25 mL of acetonitrile were added to the funnel for a second extraction. The second acetonitrile layer was added to the first. The sample was slowly concentrated on a Kuderna Danish chest until almost dry, then allowed to go to dryness at room temperature. The sample was resolvated in 0.5 mL of acetonitrile and 3.5 mL of 25 millimolar (mM) phosphate buffer, then filtered through a 0.45 µm Millex filter prior to HPLC analysis for 2,6-DAT, 2-A-4NT, 4-A-3NT, 2,6-DNT and DNT. The chromatographic conditions for this analysis are specified in Table 10. This method will be referred to as the "CRREL method."

Calibration standards for these two analyses were prepared containing concentrations ranging from approximately 250 ppm to 0.01 ppm. Stock solutions with concentrations of approximately 2000 ppm were combined and diluted to make the working standards. Standard solutions were injected, and the resultant data were used to calculate calibration curves. Calibrations were based on area, though peak height data was directly comparable. The detection limit was determined to be 0.01 mg/L.

Acid and alcohol analysis. Samples of the reactor effluent were collected and adjusted to a pH of 2 with phosphoric acid for organic acid and alcohol analysis. The samples were analyzed for methanol, ethanol, and acetic and propionic acids by GC methods supplied by the University of Cincinnati (described above). The GC conditions for these analyses are specified in Tables 11 and 12. In both methods, the samples are diluted with an internal standard containing sodium hydroxide and filtered through a 0.45 µm Millex filter before GC analysis.

For acid analysis, calibration standards were prepared containing 1, 5, 10, 25, and 50 mg/L of each acid. Standards were prepared for analysis in the same manner as samples. The internal standard solution for the acids was prepared to contain 80 mg/L butyric acid in 0.1 normal (N) sodium hydroxide solution. Standard solutions were injected, and the resultant data was used to calculate calibration curves. The detection limit was determined to be 1.0 mg/L.

For alcohol analysis, calibration standards were prepared containing 1, 5, 10, 25, and 50 mg/L of each alcohol. Standards were prepared for analysis in the same manner as samples. The internal standard solution was prepared to contain 80 mg/L n-propanol in 0.1N sodium hydroxide solution. Standard solutions were injected, and the resultant data were used to calculate calibration curves. The detection limit was determined to be 1.0 mg/L.

Ether and ethanol analysis. Samples of the reactor influent and effluent were also taken for diethyl ether and ethanol analysis. The influent samples were not pH adjusted; however, the effluent samples were adjusted to a pH of 2 with phosphoric acid. The samples were analyzed by an external standard method with the conditions specified in Table 13.

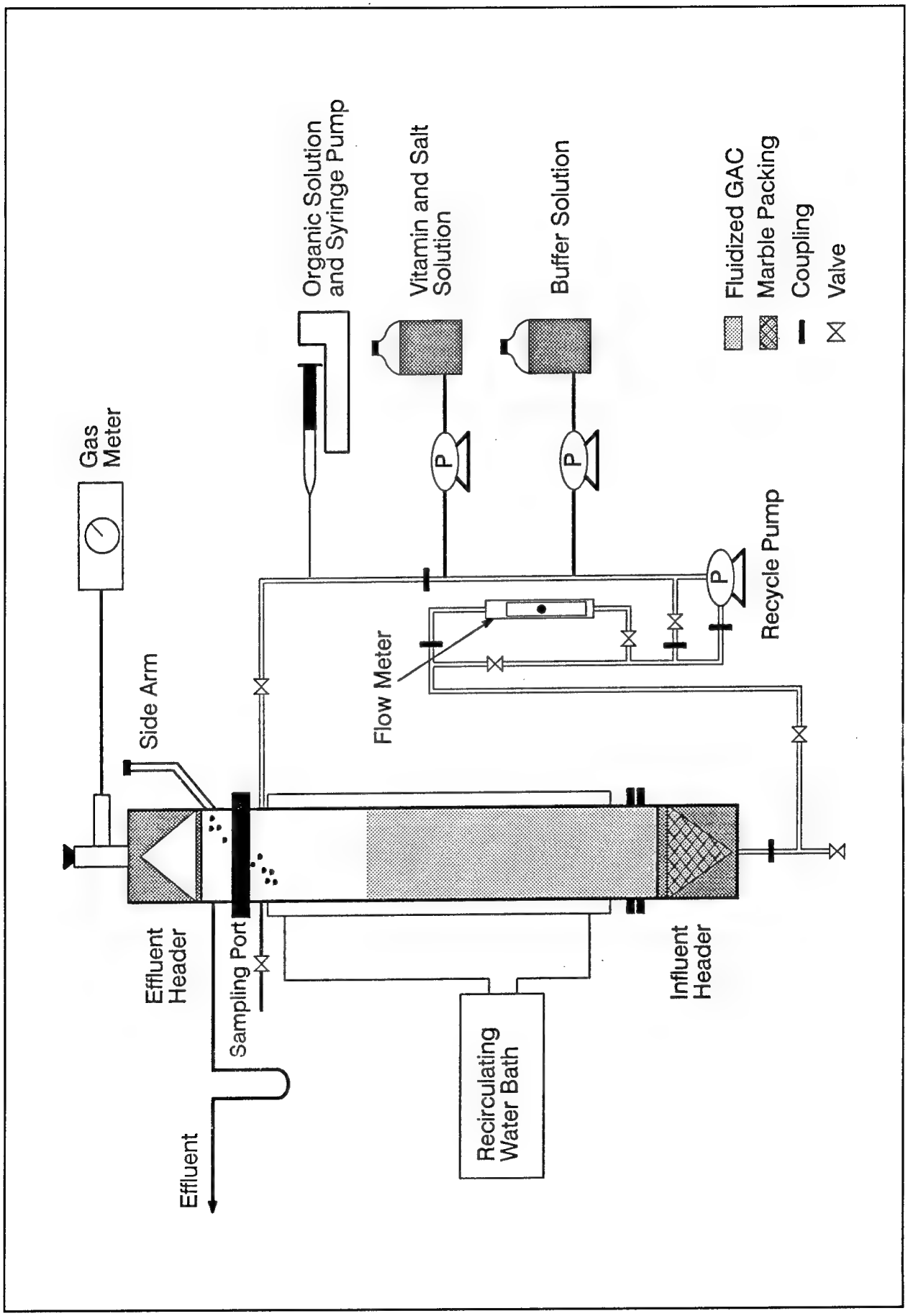

Figure 1. Anaerobic fluidized-bed GAC bioreactor.

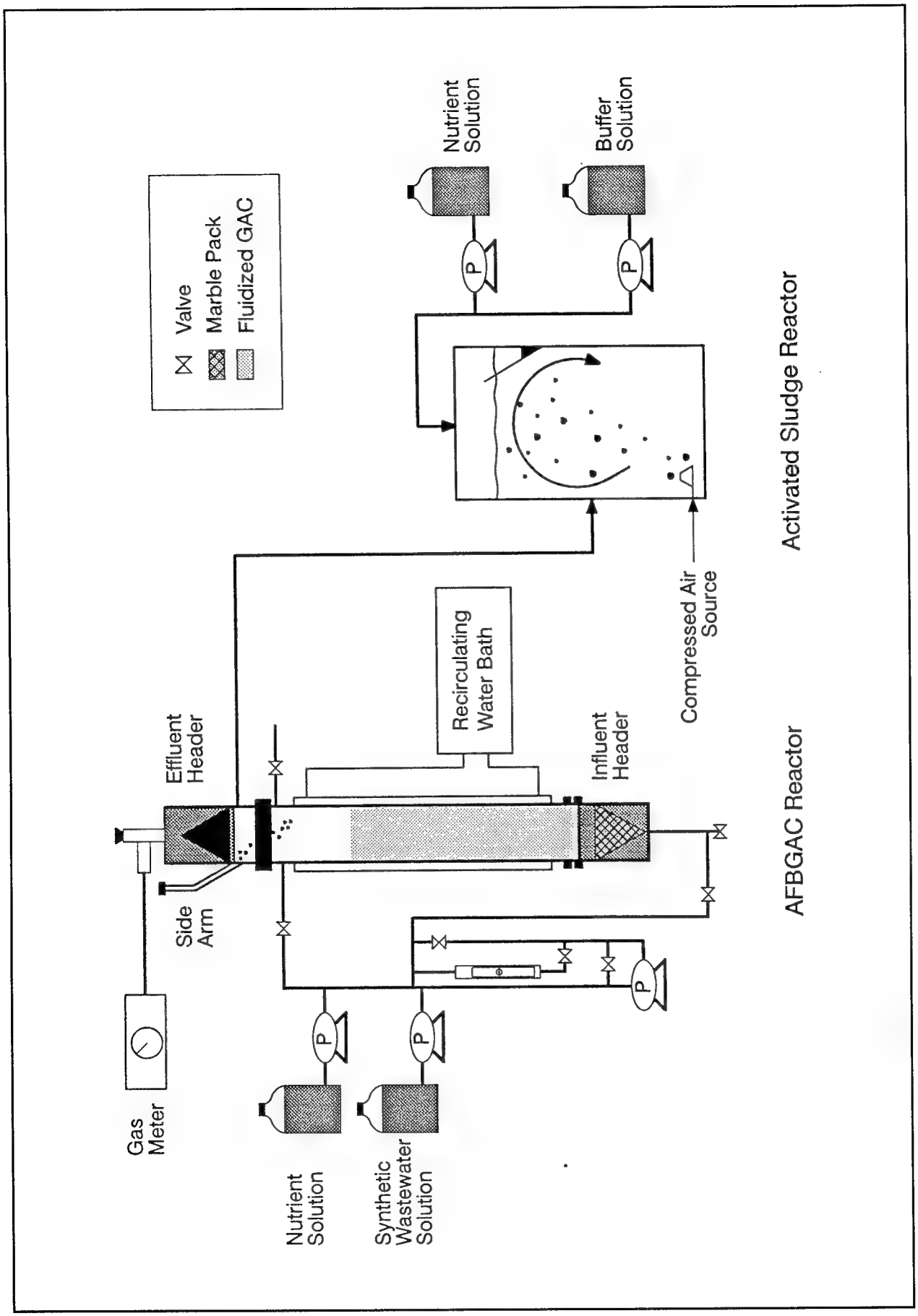

Figure 2. Two-step system schematic.

Table 1. Stock trace salt solution.

Component	Concentration (g/L)
Ammonium Molebdate ($(NH_4)_6Mo_7O_{24} * 4H_2O$)	2.08
Sodium Borate ($Na_2B_4O_7 * 10H_2O$)	1.15
Nickel Chloride ($NiCl_2 * 6H_2O$)	3.00
Manganese Chloride ($MnCl_2 * 4H_2O$)	4.74
Cobalt Chloride ($CoCl_2 * H_2O$)	2.86
Zinc Chloride	3.27
Copper (II) Chloride ($CuCl_2 * H_2O$)	2.05

Table 2. Stock salt solution.

Component	Concentration (g/L)
Trace Salt Solution	33.1 mL/L
Magnesium Chloride ($MgCl_2 * 6H_2O$)	8.13
Sodium Phosphate ($NaH_2PO_4 * H_2O$)	8.28
Potassium Phosphate (KH_2PO_4)	13.6
Ammonium Chloride (NH_4Cl)	17.0
Calcium Chloride ($CaCl_2 * 2H_2O$)	5.88

Table 3. Stock vitamin solution.

Component	Concentration (g/L)
p-Aminobenzoic Acid	0.01
Biotin	0.0039
Cyanocobalamin (B12)	0.0002
Folic Acid	0.0039
Nicotinic Acid	0.01
Pantothenic Acid	0.01
Pyridoxine Hydrochloride	0.02
Riboflavin	0.01
Thiamin Hydrochloride	0.01
Thioctic Acid	0.01

Table 4. Buffered solution.

Component	Concentration (g/L)
Sodium Carbonate (Na_2CO_3)	1.375
Sodium Sulfide (Na_2S)	0.05

Table 5. Gas chromatographic conditions for volatile fatty acids analysis.

Instrument	Hewlett Packard 5890
Carrier Gas	Nitrogen, 24 milliliters/minute (mL/min)
Oven Temperature	175 °C
Injection Temperature	250 °C
Detector	Flame Ionization
Detector Temperature	250 °C
Column*	1.83 meter (m) x 2 millimeters (mm) ID glass 80/120 Carbopack B-DA / 4% Carbowax

*Column pack by Supelco, Inc., Bellefonte, PA.

Table 6. Gas chromatographic conditions for alcohol analysis.

Instrument	Hewlett Packard 5890
Carrier Gas	Nitrogen, 20 mL/min
Oven Temperature	70 °C for 2.2 min then ramped 30° per minute up to 150 °C
Injection Temperature	200 °C
Detector	Flame Ionization
Detector Temperature	250 °C
Column*	1.83 m x 2 mm ID glass 60/80 Carbopack B / 5% Carbowax 20 M

*Column pack by Supelco, Inc., Bellefonte, PA

Table 7. Gas chromatographic conditions for DNT and degradation products analysis.

Instrument	Hewlett Packard 5890
Oven Temperature	90 °C for 2.5 min then ramped at 30° per minute to 200 °C
Injection Temperature	250 °C
Detector Temperature	250 °C
Column*	DB-1 Capillary

*Column from J&W Scientific, Folsom, CA

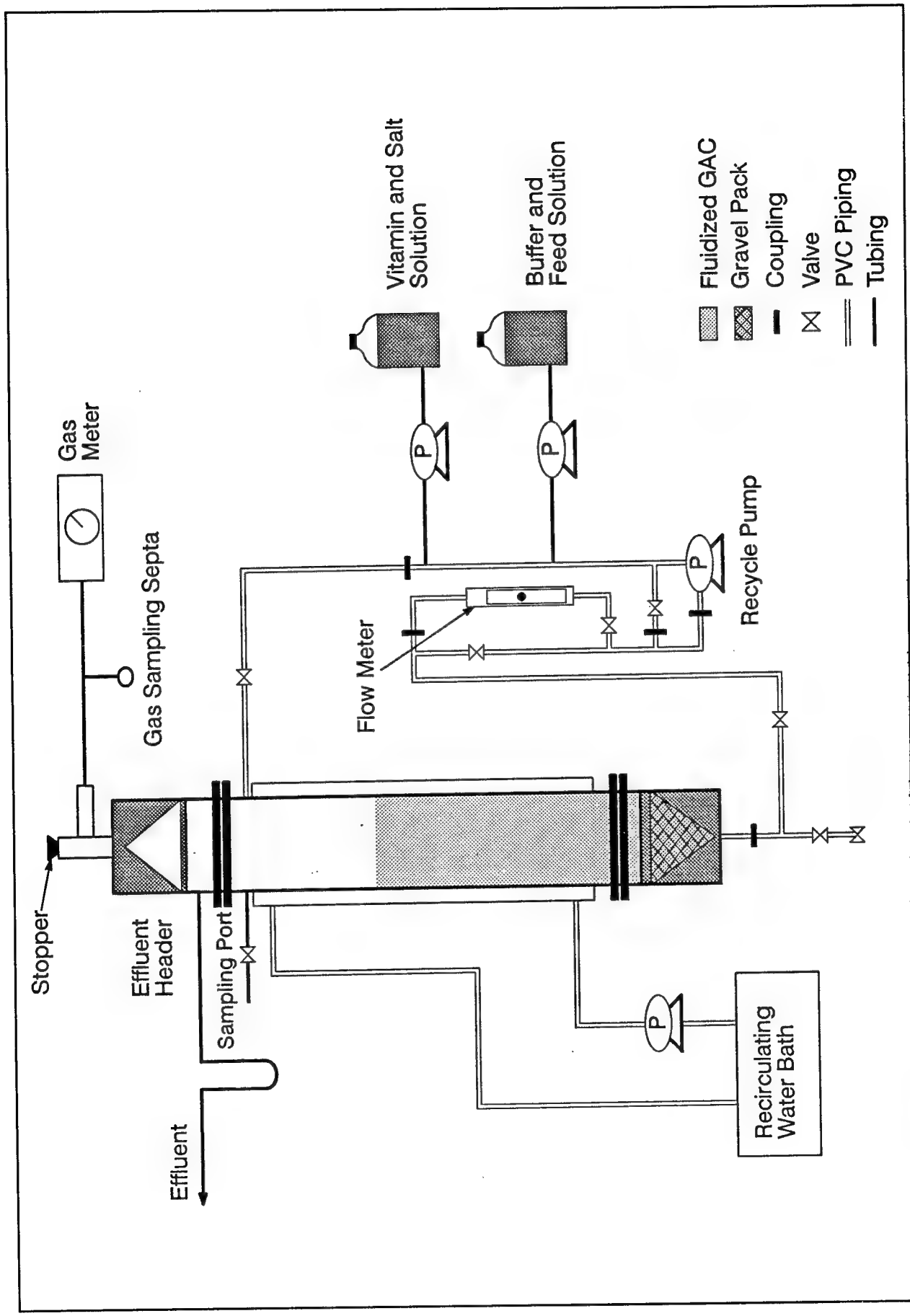

Figure 3. Bioreactor setup.

Table 8. Liquid chromatographic conditions for DNT analysis.

Mobile phase solvent	55% methanol, 45% water (v/v)
Flow	2.0 mL/min
Injection volume	200 µL
Detector	Hewlett Packard 1084 variable wavelength UV
Detector wavelength	254 nm
Column	Lichrosorb RP-18, 10µ, 25cm x 4.6mm

Table 9. Liquid chromatographic conditions for DAT analysis.

Instrument	Hewlett Packard 1090
Mobile Phase	65%/35% (v/v) 3.5 mM phosphate buffer in water/methanol
Oven Temperature	50 °C
Injection Volume	25 µL
Detector	Hewlett Packard 1040A diode array detector
Detector Wavelength	254 nm (550 nm reference)
Column	Econosphere C18 (25 cm x 4.6 mm, 5µm)

Table 10. Liquid chromatographic conditions for DNT (CRREL Method).

Instrument	Hewlett Packard 1090
Mobile Phase	65%/35% (v/v) 3.5 mM phosphate buffer in water/methanol
Oven Temperature	50 °C
Injection Volume	25 or 250 µL
Detector	Hewlett Packard 1040A diode array detector
Detector Wavelength	254 nm (550 nm reference)
Column	Econosphere C18 (25 cm x 4.6 mm, 5µm)

Table 11. Gas chromatographic conditions for acid analysis.

Instrument	Hewlett Packard 5880-A
Carrier Gas	Helium, 20 mL/min
Oven Temperature	155 °C
Injection Temperature	250 °C
Detector	Flame Ionization
Detector Temperature	250 °C
Column	6 ft x 2mm ID glass 80/120 Carbopack B-DA/4% Carbowax 20M

Table 12. Gas chromatographic conditions for alcohol analysis.

Instrument	Hewlett Packard 5880-A
Carrier Gas	Helium, 22 mL/min
Oven Temperature	70 °C
Injection Temperature	200 °C
Detector	Flame Ionization
Detector Temperature	220 °C
Column	6 ft x 2mm ID glass 60/80 Carbopack B/5% Carbowax 20M

Table 13. Gas chromatographic conditions for ether and ethanol analysis.

Instrument	Hewlett Packard 5880-A
Carrier Gas	Helium, 22 mL/min
Oven Temperature	70 °C
Injection Temperature	200 °C
Detector	Flame Ionization
Detector Temperature	220 °C
Column	6 ft x 2mm ID glass 60/80 Carbopack B/5% Carbowax 20M

4 Results and Discussion

University of Cincinnati

General Observations

Anaerobic column. The two bioreactors (Column A and Column B) at the University of Cincinnati were operated in five stages (see Table 14), with the first three stages representing periods of accelerated loading of DNT on GAC. The objective of the increased carbon loading was to determine the DNT concentration at which breakthrough would occur (that is, where DNT would be detected in the effluent). Table 15 shows the concentration of actual water-dry components in grab samples as analyzed by RAAP. Synthetic wastewater was modeled using the July 1, 1991 data from water-dry water. The initial influent DNT concentration was 2810 mg/L. Since this concentration of DNT exceeds the solubility of this compound in water, the normal feeding procedure was supplemented with a 4.0 g/day spike of finely ground DNT. Sufficient time was allowed for the DNT particles to dissolve and adsorb or biodegrade before being washed out of the column with the effluent. During Stage I of operation, which consisted of two phases, sulfate and nitrate were added to the feed of Column B at concentrations of 1000 and 250 mg/L, respectively. These were added for nutrient requirements and for maintenance of the sulfate-reducing population. On Day 89 of Stage I, the cumulative loading of DNT to the GAC reached 223 mg DNT/g carbon. This loading corresponded to an equilibrium aqueous phase DNT concentration of 0.23 mg/L (Berchtold 1993), which is well within the range of detection. Subsequently, the feed concentration of DNT was decreased to 147 mg/L, which is still above the DNT solubility concentration in water. Even though the adsorptive capacity of the carbon was overloaded with the large DNT feed, there was still no evidence of DNT in the effluent, which supports the theory that DNT biodegradation must have been taking place in the reactor.

During Stage II of reactor operation, the total flow rate into the system was doubled in order to decrease the hydraulic detention time in the reactors. During this stage, analysis of actual wastwater samples from RAAP revealed that sulfate was not contained in the wastewater (see Table 15). From these results, it was decided to discontinue sulfate and nitrate addition to Column B. After operating the systems

during Stage II for 6 weeks, DNT was still not detected in effluent samples. The DNT spike of 4.0 g/day was resumed on Day 159 to stimulate a response from the reactors.

The flow rate to the reactors was again doubled during Stage III (Day 201). During this stage the 4.0 g/day spike of DNT was continued because DNT was not yet detected in effluent samples. Also during this stage, the concentration of ethanol in the feed was set to 6000 mg/L for Column A and 600 mg/L for Column B. These ethanol feed concentrations were chosen to reflect the reported range of ethanol concentrations found in the water-dry processes in Table 15.

Toward the end of Stage III the two bioreactors started exhibiting stress signs, as manifested by increases in the effluent concentrations of volatile fatty acids, COD, and by the emergence of DNT. At this point it was felt that the objective of loading the system with DNT was accomplished, and that the systems were ready for normal operation under concentrations of DNT that were measured in field samples. A feed concentration of DNT of 110 mg/L, which is close to the solubility limit of this compound in water, was selected.

Stage IV of the study was designed to evaluate the optimal ethanol feed concentration while maintaining a constant DNT influent concentration of 110 mg/L for both bioreactors. The feed concentrations of ethanol selected for this evaluation were 6000 and 2000 mg/L for Column A, and 600, 200, and 0 mg/L for Column B. Column B was operated without ethanol for a period of 8 weeks. This resulted in showing that a primary substrate is necessary for DNT biotransformation (see following discussion on GAC extraction), so a moderate ethanol feed concentration of 600 mg/L was selected for investigation of the two-step (anaerobic followed by aerobic) system.

During Stage V, Column A was no longer used (therefore the "NA" in Table 14), and the batch-fed system behind Column B was switched to the continuous aerobic system. An influent ethanol concentration of 600 mg/L was selected for use with Column B.

After identification of DAT in the effluent, two major questions were whether DAT would persist in the environment, and whether it was more or less toxic than DNT. If DAT were easily degraded aerobically, then the use of the anaerobic GAC bioreactor as a pretreatment followed by aerobic treatment could be tested at an existing wastewater treatment plant (such as at RAAP).

The first question was addressed by adding the activated sludge treatment step at the University of Cincinnati. Limitations at the field site and time limitations did not allow this to be evaluated in this field study. Table 16 shows the steady-state concentrations of DAT through the two-step treatment process, where DAT remained

below the detection limit in the activated sludge effluent. These results strongly suggest that the two-step anaerobic/aerobic treatment process will completely mineralize DNT in the wastestream. Further work is necessary (and currently planned at the demonstration level) to determine whether the aerobic process will provide mineralization of DAT under field conditions.

The toxicity of DAT is addressed in Appendix B.

Aerobic bioreactors. There were three apparatus setups studied by the University of Cincinnati. The first used only the two columns, with no effluent treatment (this was before DAT identification). The second setup added two activated sludge batch systems following the columns (one after each anaerobic bioreactor). This aerobic system was implemented to test the further biodegradation of DAT after it was verified in the effluent. The results from the batch testing indicated complete degradation of DAT. As a result, one of the batch reactors was replaced with a continuous-flow activated sludge reactor, which is the third setup.

The 3-L batch-fed activated sludge reactors were operated for a period of 65 days. The first 20 days of operation were a period of acclimation. During this acclimation period, each of the activated sludge reactors received 1 L of effluent from the anaerobic reactors. The reactors were then allowed to utilize all the DAT before another liter of anaerobic effluent was added. From Day 20 to Day 30, 1 L of activated sludge was replaced daily with effluent from the anaerobic bioreactors. On the 31st day of operation, due to a decrease in effluent concentrations of DAT from the anaerobic reactors, the volume of replacement was increased to 1.5 L/day. After 16 days of operation at 1.5 L/day, elevated concentrations of DAT were detected in the activated sludge reactor effluents. Thus, on Day 457, the daily replacement volume of 1.0 L/day was resumed and continued through the duration of batch operation. The batch-fed activated sludge system yielded encouraging results with respect to effluent COD polishing and DAT mineralization.

Further investigation of this two-step system incorporated a continuous-flow activated sludge unit in series with Column B. Continuous operation commenced on Day 597 when the reactor was seeded with the acclimated mixed liquor from the batch study. Additional mixed liquor from a local municipal wastwater treatment plant was supplied to thicken the sludge. The activated sludge system was operated as a semi-batch system for the first week, receiving increasing volumes of anaerobic reactor effluent daily. Initially, only the anaerobic reactor effluent and nutrients were supplied. Final effluent DAT levels from the activated sludge system persisted in the detectable range until a pH buffer was provided. Effluent levels of DNT and its biodegradation products were consistently below detection limits thereafter.

Approximately 1.2 L of mixed liquor was wasted each day to maintain a sludge age of 8 days.

Figure 4 compares the actual effluent concentration of DNT from the bioreactors to the predicted effluent concentration assuming no biotransformation (only adsorption) of the compound. Detection of DNT in the effluent occurred during Stage II, and its concentration in the effluent peaked at 1.8 mg/L at the end of Stage III. The corresponding predicted DNT effluent concentration of 100 mg/L indicated that biotransformation of the compound was well underway during the first two stages of the experiment. After the DNT spikes were discontinued at the beginning of Stage IV, the effluent concentration of DNT stabilized and decreased below the effluent quality standard of 113 µg/L.

Weekly COD balances on both reactors are shown in Figures 5 and 6. This data shows the overall effectiveness of the bioreactors relative to effluent COD and the effectiveness of the transformation of the majority of that COD to methane gas. The effects of the sulfate addition on Column B during Stage I are shown in Figure 6; the difference between the methane + effluent COD and sulfate + methane + effluent COD represents the COD removed through sulfate reduction. This relatively small difference in the COD balance demonstrates that the sulfate and nitrate addition to the column did not have a major impact on column performance.

The difference between the influent COD and the methane + effluent COD in Figures 5 and 6 represents the sum of the fraction of the influent COD adsorbed on the GAC plus the COD equivalent of the attached biomass. The data in both Figures 5 and 6 exhibit an increase in the mass of COD in the effluent of the bioreactors during Stage III of operation. This was attributed to the inability of the systems to handle the spike loading of the DNT through side-arm addition when the flow increased. Once the process of side-arm spike addition of DNT was discontinued on Day 249, the two bioreactors appeared to stabilize.

Figures 7 and 8 present how the concentrations of the volatile fatty acids (acetic acid and propionic acid) and the alcohols (methanol and ethanol) measured in the effluents from the two bioreactors vary over time. Effluent ethanol concentrations were monitored to confirm the utilization of the alcohol present in the feed. Although methanol was not fed to the bioreactors, it was routinely found in the effluents. As can be seen in both Figures 7 and 8, the effluent concentrations of ethanol and methanol were stable and consistently below 0.47 mg/L and 0.91 mg/L respectively.

Acetic acid and propionic acid are known intermediates of the anaerobic transformation (methanogenesis) of ethanol to methane gas. Consequently, the effluent

concentrations of these volatile fatty acids were monitored to confirm the conversion of ethanol to volatile acids, as well as the conversion of volatile acids to methane gas. During Stage III, Figure 7 shows an increase in the effluent concentrations of acetic and propionic acids. The failure of the bioreactor to more efficiently convert volatile acids to methane represents a sign of stressed conditions, which was attributed to the DNT spikes and the increased load of ethanol to the system. Similar responses were not observed from Column B (Figure 8), because this reactor was not subjected to the increased load of alcohol. After the spikes were discontinued, the effluent concentrations of volatile acids stabilized.

The amount of biomass accumulating on the GAC in Column A increased to extreme proportions due to the high ethanol feed concentrations (6000 mg/L). This increase in attached biomass clogged the recirculation system on Day 230, which resulted in collapse of bed fluidization and the emergence of substantial levels of acetic acid and propionic acids in the effluent. To keep the GAC and biomass fluidized and still maintain the level of the bed below the recirculation withdrawal port, it was necessary to remove approximately 40% of the GAC in Column A on Day 383. It was necessary to further remove another 10% and 50% of the remaining GAC in Column A on Days 500 and 571 in order to maintain stable reactor expansion and performance. This left Column A with approximately 27% of the original 1.0 kg of GAC it was charged with on Day 0. The GAC that was removed from Column A was not replaced with fresh carbon, because the reactor appeared to continue processing the influent organic compounds successfully. The data in Table 17 summarizes the quality of the effluent from the two bioreactors. Table 18 summarizes the effluent concentrations of DNT and its transformation products obtained during Stage IV of operation (DNT, 2-A-4-NT and 4-A-2-NT results were not available for 600 mg/L). At all feed ethanol concentrations except 0 mg/L, the effluent concentrations of DNT fell below the proposed NPDES limits of 113 µg/L. The 0 mg/L feed ethanol concentration failed to meet this limit. This reinforces prior findings that a substrate is necessary to co-metabolize DNT under anaerobic conditions.

Table 17 also depicts the percent of influent COD that was transformed to methane gas and that portion that persisted in the aqueous effluent. The data for Column A shows that for both influent concentrations of ethanol of 6000 and 2000 mg/L, the sum of the fraction of influent COD converted to methane plus the fraction of that COD that persisted in the effluent was consistently smaller than the feed COD. The difference was attributable to the COD equivalent of the biomass retained in the bioreactor. This appreciable amount of accumulated biomass led to the need for partial wastage of the bioreactor medium described earlier. On the other hand, the COD material balances on Column B reveal that the sum of effluent COD plus the COD equivalent of the methane produced was consistently larger than the feed COD.

This is attributable to the release of preadsorbed COD from the bioreactor when the influent COD concentrations were decreased. A breakdown of known contributors to effluent COD is found in Table 19. Effluent COD due to DAT concentrations represents the majority of measured COD. In the case of the lower ethanol feed concentrations, over 90% of the effluent COD is due to DAT.

Even though the columns were able to biodegrade the DNT, the bulk of the degradation products was made up of DAT. Figure 9 illustrates the effluent DAT from both reactors for the different ethanol feed concentrations during the last 80 days of Stage IV. The DAT theoretical line represents the amount of DAT expected in the effluent if all influent DNT (110 mg/L) were transformed to DAT. This figure shows that for both columns, the effluent concentration of DAT was very close to the expected value. The concentration of DAT did decrease appreciably below the expected value after ethanol was deleted from the feed. This can be attributed to a cessation of the transformation of DNT to DAT resulting from the removal of ethanol from the feed. The cessation of DNT biotransformation is evidenced by the increased breakthrough on Column B and the carbon extractions described in the following paragraphs. Unutilized DNT competes for adsorption sites on the GAC surface with preadsorbed DAT and causes the continued release of DAT (by displacement from the GAC surface) from the reactor even though the formation of DAT has stopped.

Isotherms run at 35 °C in the absence of molecular oxygen suggest that for the liquid concentrations measured in the bioreactor effluent after ethanol addition ceased, GAC has a higher capacity for DNT than for DAT . This can clearly be see in Figure 10, where the data has been plotted using the Freundlich parameters. A comparison between DNT and DAT of equilibrium solid (adsorbed) phase loading shows that the GAC had approximately the same capacity for either compound although the liquid phase concentration of DAT was almost 80 times greater.

DAT effluent levels exceeded the DNT feed equivalent after ethanol feed was resumed on Day 611. This was due to the appreciable levels of DNT that had been adsorbed onto the carbon that were now being desorbed and biotransformed. Twenty days after the ethanol feed was resumed, DNT effluent levels dropped below detectable limits; traces of nitro-amino intermediates disappeared within 35 days.

GAC extractions. Periodically during this study, GAC samples were withdrawn from both bioreactors and analyzed for adsorbed DNT and its anaerobic biotransformation intermediates. A summary of the results of these extractions is shown in Table 20. Even during the periods of high addition rates of DNT to the GAC during the initial period of this study, all the DNT was converted to DAT, 4-A-2-NT, and 2-A-4-NT.

Adsorption of DNT was not detected on the bioreactor GAC for all phases of study except for the period when ethanol was withdrawn from the feed.

The removal of ethanol from the feed to Column B appeared to have caused an appreciable reduction in the rate of transformation of DAT. A limited degree of transformation appears to have continued while utilizing preadsorbed organic matter from the GAC as a primary carbon source. This becomes evident from Table 17 where it can be seen that the Column B COD was more than double the influent COD. The excess DNT that had been adsorbed had started to accumulate on the carbon. DNT was again not detected on the bioreactor GAC once ethanol feed was resumed.

The decrease in the mass of DAT stored on the GAC in both bioreactors during Stage IV is attributable to the lower concentration of DNT fed to the columns during this stage of operation, since the GAC DAT concentration is a function of the DNT feed concentration. When the feed concentration of DNT was higher during the earlier stages of operation, a significant amount of DAT was stored on the GAC. When the influent concentration of DNT was decreased during Stage IV, the DAT concentration would also decrease, causing stored DAT to desorb from the GAC to maintain equilibrium with the lower liquid concentrations of DAT.

Activated sludge process. The high concentrations of DAT in the bioreactor effluents caused considerable concern as to the effectiveness of the anaerobic process in reducing the toxicity of the wastewater. Since DAT is a suspected carcinogen, the presence and treatment of this compound needed to be addressed. Several options were considered to improve final effluent quality and it was decided to test the treatability of the effluent using two batch-fed activated sludge reactors. These reactors were chosen based on their ready availability and on the fact that RAAP already had an aerobic wastewater treatment facility on site. In such a treatment scenario, the bioreactor would be used as a pretreatment process to greatly reduce wastewater COD and transform DNT to DAT. Then the second-stage activated sludge process would polish the effluent COD while mineralizing the DAT.

The data in Figure 11 represents a batch test evaluating the rate of biodegradation of DAT in the two batch-fed activated sludge units. One L of effluent from the anaerobic columns was added daily to 2 L of activated sludge and aerated. The figure represents the degradation of DAT over time. Within nine hours, the concentration of DAT in the effluent was below detection. The cycle of settling, supernatant decanting, and feeding was repeated daily, and a summary of the data for this operation is presented in Table 21. The average effluent concentrations of DAT were stable and consistently below 0.85 mg/L. Under most instances, the effluent DAT concentrations fell well below detectable limits. Thus, post-treatment of DAT in an aerobic system appeared feasible.

A continuous activated sludge system in series with Column B was implemented shortly before ethanol feed was resumed at 600 mg/L. Once a buffered solution was supplied to maintain nitrifier activity, effluent levels of DAT dropped below the detection limit. Additional evidence of DAT mineralization is the weekly nitrogen balance shown in Figure 12. Anaerobic influent nitrogen sources included ammonia and DNT. Influent ammonia in the nutrient feed solution was reduced on Day 773 to give a clearer picture of the nitrogen balance. Effluent nitrogen was measured as ammonia and DAT. This is accounted for as the sum of nitrate in the final effluent plus 12% of daily wasted volatile suspended solids from the activated sludge reactor (Metcalf and Eddy, Inc. 1991). Good closure in the nitrogen balance suggests that the DAT is completely mineralized.

The weekly COD balance (see Figure 13) indicated that the activated sludge system fulfilled its second goal of final effluent polishing with respect to COD. The influent COD was 10 g/day after primary substrate addition was resumed on Day 611. Most of this was converted to methane gas, but the anaerobic effluent COD might still exceed 200 mg/L. Final effluent COD was consistently less than 35 mg/L (0.27 g/day) with use of the aerobic system. The difference between anaerobic reactor effluent and final effluent can be attributed to biological growth in the activated sludge unit. Steady-state effluent quality has already been presented in Table 16.

Radford Army Ammunition Plant

General Observations

One of the bioreactors from the University of Cincinnati (without an activated sludge system) was transported and installed at RAAP in September 1992. It was jointly operated by both University of Cincinnati and RAAP personnel until the start-up phase was completed and RAAP personnel were comfortable with the operating procedures. At startup, wastewater containing DNT from an actual water-dry operation was used in the feed. This was the first time actual strength wastewater was used in this reactor. The influent concentrations of DNT, ethanol, ether, and COD varied widely. The wastewater was collected by taking samples off the top of the water-dry process during actual propellant production. The concentrations encountered at RAAP are shown in Table 22. Wide fluctuations in the influent concentration caused operational problems, which will be discussed later.

The reactor stayed at RAAP from September until April 1993 and was fed water-dry water of varying strengths during that time period. The University of Cincinnati provided the vitamin solution throughout the course of the reactors' stay at RAAP.

The data collected included date, time, amount of buffer solution in feed tank, amount of nutrient solution in feed tank, pH of the reactor, gas meter reading, water bath temperature, air temperature, and GAC level. The values calculated from the measured data include amount of buffer solution used, amount of nutrient solution used, and amount of gas produced. Both measured and calculated values can be found in Table 23. RAAP had no major problems maintaining the column during the first two months.

In January 1993 the testing done on the reactor expanded to include an increase in the process flow rates to the system. This test period lasted for three months. There were four flow rates to be tested: 6, 9, 12, and 18 L/day. The flow rate was increased at the beginning of the test period from 4 to 5 L/day to approximately 6 L/day (in mid-January). The same type of data that was collected in the first test period was also collected and calculated during this period, and can be found in Table 24.

At the end of January, the carbon bed level began requiring adjustment, which indicated that fluidization was not remaining constant as it had in the previous test interval. By the middle of February, parts of the carbon bed were rising to the top of the reactor as one large plug and trapping the gas produced by the microorganisms beneath it. This resulted in operation personnel having to physically break apart the carbon mass on a daily basis. With the rising of the carbon bed above the fluid level, pieces of the granular carbon were being pulled into the recycle lines, ground up by the centrifugal pumps, and returned to the system as powdered carbon. Parts of the carbon bed were also floating to the top due to biomass growth.

When the carbon bed began fluctuating, the fluid above the carbon bed, previously clear, started to cloud with carbon and biomass. It became almost impossible to read the GAC level because the liquid above the carbon blended with the color of the carbon. The liquid above the carbon did not begin clearing up until the end of the three-month period, which indicated that column fluidization had not yet been achieved. Column oscillation was expected after the initial change in flow, but it was also expected to recover much faster than it did (based on the fast recovery after the initial move to RAAP). As a result, the flow was not increased in the increments originally planned. The flow was eventually increased in March (middle and end), but in smaller increments than what was originally planned for (up to approximately 7 L/day and then up to approximately 8 L/day).

First, personnel attempted to return the column to a stable state by filtering off the unsettleable powdered carbon and "clearing" the effluent liquid above the bed, so that the fluidization level could be seen and correctly maintained. When that proved insufficient, the reactor was disassembled in mid-February by Hercules and CERL

personnel and the reactor and all adjoining lines were cleaned and filtered of the unsettleable particles. In addition, the GAC was also washed of powdered carbon. This required complete shutdown of the system for several hours. It was hoped that this cleaning would rid the system of enough ground-up carbon that the GAC fluidization level would again be visible, but the system remained cloudy through the end of the test period.

Another important operating parameter that had remained constant during Phase I was pH (see Figure 14). This began varying wildly in Phase II due to a massive increase in ethanol loading (see Figure 15), which resulted in the formation of acids in the system, and hence a higher pH. In contrast to the first two months, where there were very few deviations from the optimum pH realm (7.2), the pH ranged from a low of 5.4 to a high of 9.6 during the first month of Phase II. However, during the last two months it stabilized around optimal conditions, although it began varying again during the last week of operation.

Figure 16 is a comparison of gas production to influent COD and effluent DNT levels. During the first two months of field operation, gas production tracked very well with influent COD. When the pH dropped drastically during Phase II, gas production was no longer proportional to influent COD. This indicates a disruption in the bioactivity.

Figure 17 shows the influent COD compared to the influent and effluent DNT observed during the field study. The average effluent DNT is highly affected by the one high data point at 25 mg/L, when gas production was low and COD was high, indicating disruption of bioactivity. If that data point is eliminated, the anaerobic pretreatment step would meet the proposed NPDES permit levels..

In general, the problems in Phase II of the study are attributed to the simultaneous increase in flow and increase in ethanol concentration. The mass loading is the product of flow and concentration, thus the overall mass loading increased much more than was expected from a change in flow alone. This increase was more than the biomass could handle. Automated pH control could have solved this problem, but that was unavailable for this system, although it will be available in the planned demonstration.

General Evaluation of Technology (Phase I)

In Phase I, water-dry water was buffered and placed in an influent reservoir. The "buffered solution" is the water-dry water with buffers added, and is the influent in the following discussion. The quantities of buffered and nutrient solutions are provided in Figure 18. The quantity of buffered solution fed consistently remained in the range

of 4 to 5 L/day, with one low flow of 3.4 L/day on Day 16 and two high flows of 5.69 L/day on Day 21 and 6.34 L/day on Day 59. The quantity of nutrient solution fed generally remained in the range of 0.5 to 1.0 L/day, with a low flow of 0.30 L/day on Day 35 and a high flow of 1.38 L/day on Day 62. Gas production (measured as methane) was initially greater than 1 L/day until after Day 13, when gas production dropped to as low as 0.19 L/day (cause unknown). On Day 23, gas production recovered to the 2 to 4 L/day range (this recovery does not correlate with the addition of sodium sulfide to the nutrient solution, which occurred six days later on Day 29) and remained there until Day 52. From Day 52 on, gas production was generally in the range of 1 to 2 L/day.

The pH of the reactor's contents during the evaluation are represented in Figure 14, which shows that the pH was maintained generally in the 7.0 to 7.2 range with minor deviations.

Sampling and analysis of the column influent and effluent were also performed (Table 25). The analysis of DNT, alcohol, ether, and COD of both the column influent and effluent were performed when influent feed solutions were changed, or when needed to supplement data from other analytical methods. Additionally, analysis for fatty acids and DNT biodegradation byproducts (CRREL method, Table 26) was performed weekly.

The analytical results for the influent DNT and the effluent DNT and DAT are represented in Figure 19. It should be noted that the results for DNT are based on the RAAP method. The identity of the DAT is based on the CRREL method and has been confirmed by gas chromatography and mass spectroscopy (GC/MS) at the HML/ HWRIC. During the evaluation, the influent DNT generally remained in the 120 to 140 mg/L range, while effluent DNT was either not detected or was below 0.4 mg/L. However, DAT analysis indicated a surprisingly high concentration of DAT (63.46 to 107.46 mg/L) in the effluent, with the concentration increasing as the evaluation progressed. This was confirmed by the University of Cincinnati in the latter part of their study.

The analytical results for the influent alcohol and ether present in the buffered solutions indicated variable feed concentrations (Figure 20). The feed varied from 60 to 2970 mg/L for the alcohol and 0 to 400 mg/L for the ether. The resultant effluent was consistently low in both alcohol and ether, indicating that the system could handle significant fluctuations in the feeding of organics.

Measurement of the influent and effluent COD is represented in Figure 21. The influent COD stabilized in the range of 2000 to 3000 mg/L on Day 36, and the effluent COD stabilized in the range of 500 to 600 mg/L.

The CRREL analytical results of byproduct analysis of the reactor effluent are represented in Figure 22 and Table 26. Analysis for 2,6-DAT, DAT, 2-A-4-NT, 4-A-2-NT, 2,6-DNT, and DNT indicated that the DNT was biotransformed, with DAT as the only significant byproduct.

Hydraulic Loading Evaluation (Phase II)

The quantities of buffered and nutrient solutions are shown in Figure 23. The quantity of buffered and nutrient solutions fed daily was varied during the evaluation in an attempt to determine the maximum hydraulic capacity of the GAC anaerobic reactor. On Day 11 of Phase II, the combined flow rates were increased to achieve a rate of 9 L/day, and on Day 18 the evaluation was initiated. A significant fluctuation occurred on Days 27-28 for the buffered solution; however, it is believed that one data point was recorded incorrectly, because averaging the two points results in no fluctuation. A similar fluctuation occurs for the buffered solution on Days 36-39. On Day 43, both flow rates were reduced to permit the GAC anaerobic reactor an opportunity to recover. Until Day 70, when a power failure to the building resulted in virtually no flow for 24 hours, the flow rates were relatively consistent at 5 to 6 L/day for the buffered solution and 1 L/day for the nutrient solution. The process flow rate was increased in approximately 25% increments on Days 71 and 81. The process rates through these periods was fairly consistent.

The quantity of gas produced (measured as methane) is shown in Figure 24. Initially, gas production responded to the increased processing rate for the buffered and nutrient solutions with extremely high production rates (approximately 25 L/day); however, as the column became plugged and lost fluidization, gas production decreased and became variable. When processing rates were again increased after the problems with the column had been corrected (Day 70), gas production again increased to greater than 25 L/day. After the processing rate had been increased by 50% and a second power failure occurred, gas production again dropped and became variable.

As can be observed from Figure 15, the pH of the GAC anaerobic reactor was maintained generally in the 7.0 to 7.2 range except when problems occurred. On Day 29, the pH reached 9.2 due to precipitated sodium carbonate reaching the column from the buffered solution feed. On Day 33, the plugging of the column and loss of fluidization resulted in decreased biodegradation capability, incomplete degradation, and a drop in pH. The high pHs that were recorded were due to overcompensation by

manual adjustment of the pH with addition of sodium carbonate and/or sodium hydroxide. After the processing rate was reduced, the pH stabilized until the power failure on Day 90 and stabilized again until the last day of the experiment, when organic loading essentially doubled.

Sampling of the column influent and effluent was also performed. The analysis of DNT (HPLC method), alcohol, ether, and COD of both the column influent and effluent is contained in Table 27. Analysis for fatty acids (RAAP method) in the effluent is also contained in Table 27. Additionally, the results from the CRREL DNT analysis for samples are contained in Table 28.

The analytical results for the influent DNT and the effluent DNT (HPLC method) and DAT (CRREL method) are shown in Figure 25. During the evaluation, the influent DNT generally remained in the 120 to 175 mg/L range except from Day 60 through Day 70, when it dropped as low as 49.6 mg/L DNT. The concentration again dropped to 100.0 mg/L DNT on the last day of column operation. DNT was found in high concentration in the effluent on Day 32 (25.0 mg/L), and sporadically in smaller concentrations for the remainder of the evaluation (Table 26). DAT analysis was not performed continuously during the evaluation, as evidenced by the gaps in the data. The lack of analysis was due to interferences from powdered carbon and biomass in the effluent. When samples were again collected at roughly Day 40, DAT concentration was significantly lower than 50% of the influent DNT. Samples were collected from Day 80 to the end of the evaluation and again indicated greater than 50% removal for the period. Near the end of the evaluation, a high organic shock occurred on Day 100 due to the addition of new wastewater (27,725 mg/L COD, Table 26), but as can be observed, the microorganisms were able to recover by Day 103. The final sample indicated the lowest DAT concentration, recorded at 13.1 mg/L, which was less than 25% of the influent DNT.

The analytical results for the influent alcohol and ether present in the buffered solutions indicated variable feed concentrations (Figure 26), which would be expected for actual field operations. The feed varied from 900 to 4800 mg/L for the alcohol, with the exception of the last days of the evaluation, where the concentration climbed to over 9000 mg/L. The feed varied from 70 to nearly 1000 mg/L for the ether, with the exception of the last days of the evaluation, where the ether concentration reached a high of over 2000 mg/L. The resultant effluent was consistently low in alcohol, and it appears that the ether passed through the column with minimal, if any, biodegradation. This data indicates that the system could handle significant fluctuations in the feeding of organics such as alcohol, but is apparently unable to biodegrade the ether.

Measurement of the influent and effluent COD is shown in Figure 27 (see Table 26 for data). The influent COD was generally in the range of 5000 to 15000 mg/L, with a few exceptions. The data from Days 21 through 25 appear to be incorrect, because the alcohol concentration alone should produce higher results. Additionally, results at the end of the evaluation are higher, due to the high alcohol and ether concentrations previously discussed. The effluent COD was generally in the range of 350 to 5600 mg/L (excluding Days 21 through 25), with the high CODs occurring during periods of stress to the column.

The results from the fatty acids/alcohols analysis for the GAC anaerobic reactor are represented in Figure 28, providing a reliable assessment of microorganism stress or overload. Acetic and propionic acids were detected after Day 32 (when there was loss of fluidization) and were detected at varying quantities throughout the remainder of the evaluation. No methanol was detected, but alcohol was detected in varying quantities after Day 32.

The CRREL analytical results of byproduct analysis of the effluent from the GAC anaerobic reactor are shown in Figure 29. Figure 30 excludes DAT so that the quantities of the other by-products are more evident. Analysis for 2,6-DAT, 2-A-4-NT, 4-A-2-NT, 2,6-DNT, and DNT indicates that the DNT was biotransformed with DAT as the only significant byproduct. This can be further seen in Figure 31, where the molar concentrations of DNT and DAT are shown. During stable operation, there is almost a one-to-one conversion of DNT to DAT.

The latter half of the field study was designed to increase the flow rate, thus decreasing the hydraulic retention time. A minimum safe operating time would result in the least capital cost for facility construction. However, at the same time the flow rate was increased, there was a dramatic increase in the influent COD concentration. The increased concentration occurred because a fresh batch of propellant was being processed, and the influent to the bench scale reactor was drawn off the top of the batch water-dry process. The net result from an increase in the flow rate plus a simultaneous increase in the organic concentration was a dramatic increase in COD loading to the bioreactor. Because anaerobic degradation involves a variety of organisms, all involved in a symbiotic relationship, pH will drop when one group cannot keep pace with another. Under these circumstances of high ethanol loading, the methanogens could not keep pace with the acid formers, so both the pH and gas production dropped.

Two changes were made in an effort to cope with the increased load. First, base was manually added to the feed solution to help maintain the pH within an acceptable

range. Second, the flowrate was reduced. Table 29 shows the flow rates for the entire field study.

During the period of very high influent ethanol, when the pH was uncontrollable, the balance between DNT and DAT was not good. Between February 18 to March 18, operational problems discussed above interfered with the analysis of DAT. However, a consistent feature of the molar balance (Figure 31) shows that DAT was displaced when the bioreactor was unstable and gas production was low. When the bioreactor was first moved to the field, there was a lag between the installation and recovery of gas production. A large concentration of DAT was observed in the effluent just after the move. The large DAT concentrations suggest that DNT was displacing DAT from the carbon surface until the bioactivity recovered. Again in January, when the flowrate was increased (increasing the mass loading of both DNT and COD to the bioreactor), DAT was displaced from the bioreactor. Overall, when the bioreactor was stable, the field results were consistent with the laboratory results, and DAT was the principal by-product.

The ultimate mineralization of DAT was not addressed in the field study, but it was in the laboratory. As before stated, the information in Table 16 suggests that DAT is effectively mineralized in the aerobic system, because it remained below detection levels.

Actual operation should occur under the conditions experienced in the September to November time frame. During this period, wastewater was collected from water-dry operations nearing the end of the batch processing. Although the ethanol and ether concentrations were much lower at this time, DNT concentrations remained near 140 mg/L because DNT is not volatile. Under these conditions, DNT is expected to be reduced to DAT. This did occur for the first three months of the field study, as shown in Figure 31.

Table 14. Column A and B mode of operation and operating parameters (influent concentrations).

Stage	Operating Period	Day	Q, L/d	2,4-DNT, mg/L	Ethanol, mg/L A/B	Mineral Ether, g/L A/B	Sulfate/ Nitrate mg/L B
I	day 36-115	36 89	1.5 1.5	2810 147	4165/4165 4165/4165	123/123 123/123	1000/250 1000/250
II	day 116-200	116 159	3.0 3.0	147 1480	4165/4165 4165/4165	123/123 123/123	0/0 0/0
III	day 201-249	201	6.0	776	6000/600	166/31	0/0
IV	day 250-585	250 417 526	6.0 6.0 6.0	110 110 110	6000/600 6000/200 2000/0	166/31 166/0 0/0	0/0 0/0 0/0
V	day 586-900	586	6.0	110	NA/600	Ethyl Ether NA/100	0/0

NA = Not Applicable

Table 15. RAAP water-dry water components.

Component	Reported (7/1/91), mg/L	Measured (12/13/91), mg/L
2,4-Dinitrotoluene	3 - 404	90 - 100
Ethanol	10 - 9310	629 - 640
Mineral Ether	1.3 - 960	ND
COD	3 - 8125	1409 - 1548
Sulfate/Nitrate	1000/250*	0/ND

* Average of values found in literature.

Table 16. Steady-state performance of the two-step system.

Parameter	Influent	Anaerobic Reactor Effluent	Final Effluent
COD, mg/l	1600 (55)	207.0 (34.1)	22.7 (7.0)
DNT, mg/l	110	ND	ND
DAT, mg/l	0	75.77 (4.44)	ND
Ammonia Nitrogen, mg/l	20	19.9 (2.6)	0.18 (0.29)
Nitrate Nitrogen, mg/l	0	ND	22.7 (1.0)

ND = Below detection limit
Standard deviation is represented in parenthesis

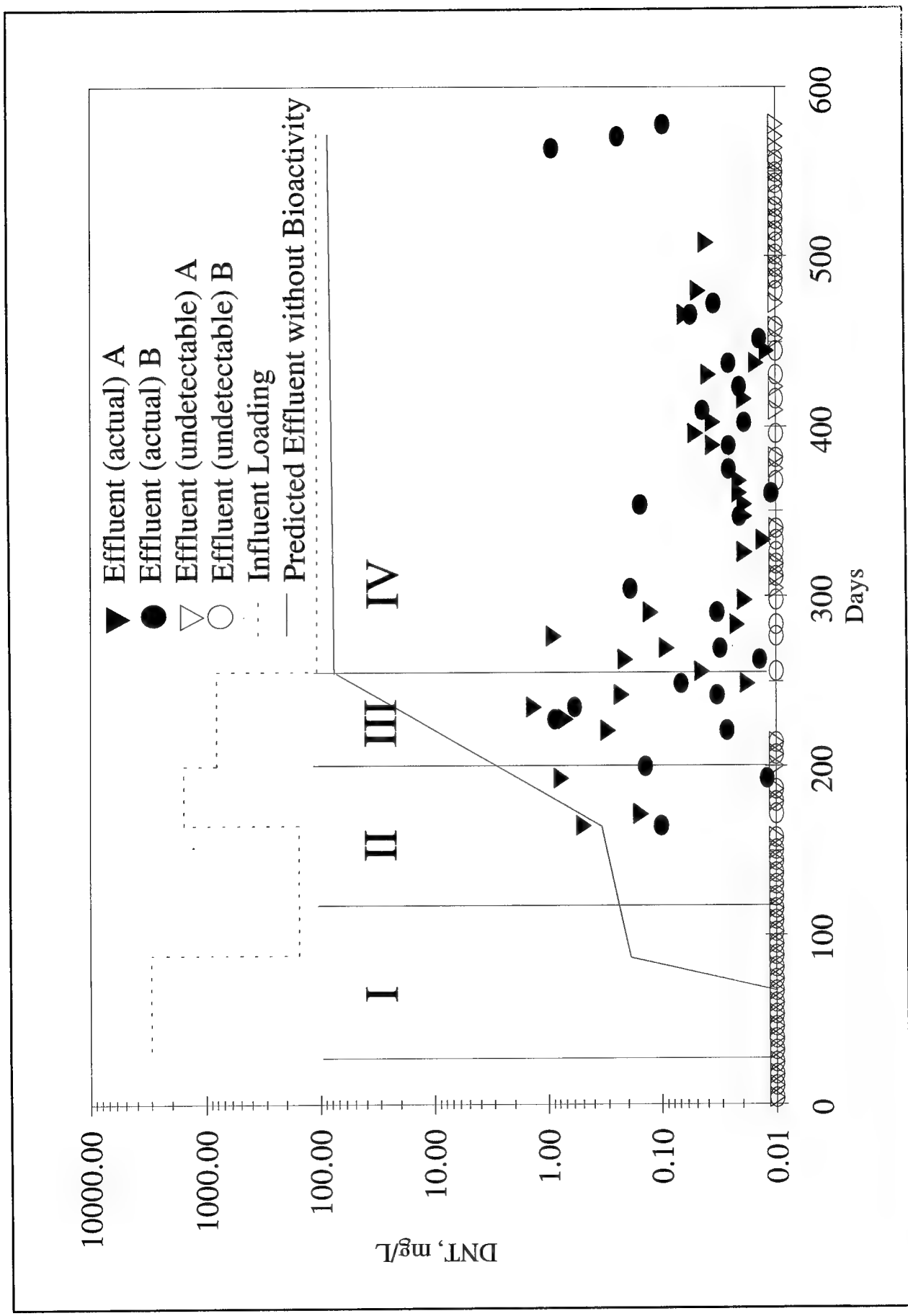

Figure 4. Influent, effluent, and predicted effluent DNT concentrations—Columns A and B.

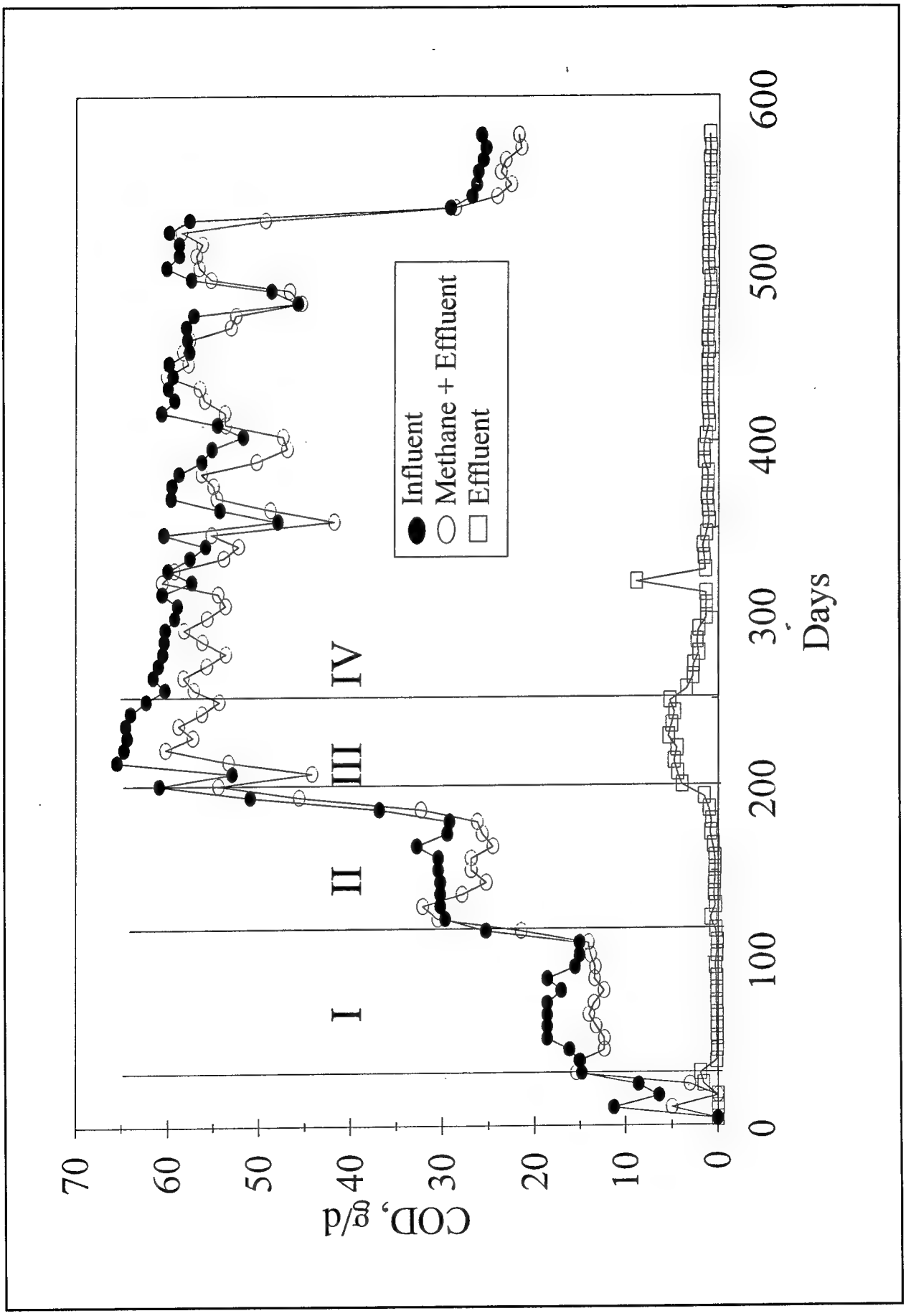

Figure 5. COD balance—Column A.

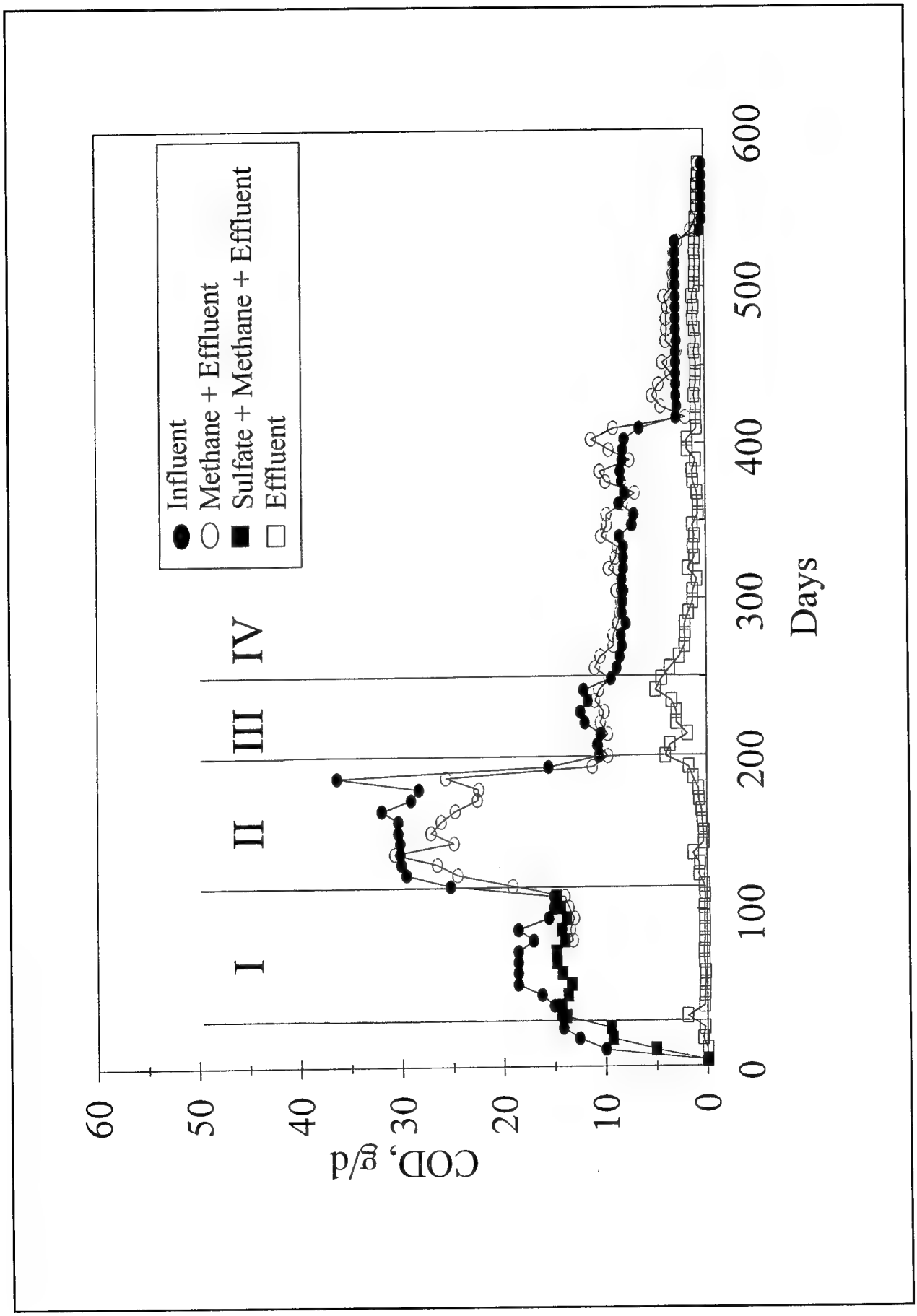

Figure 6. COD balance—Column B.

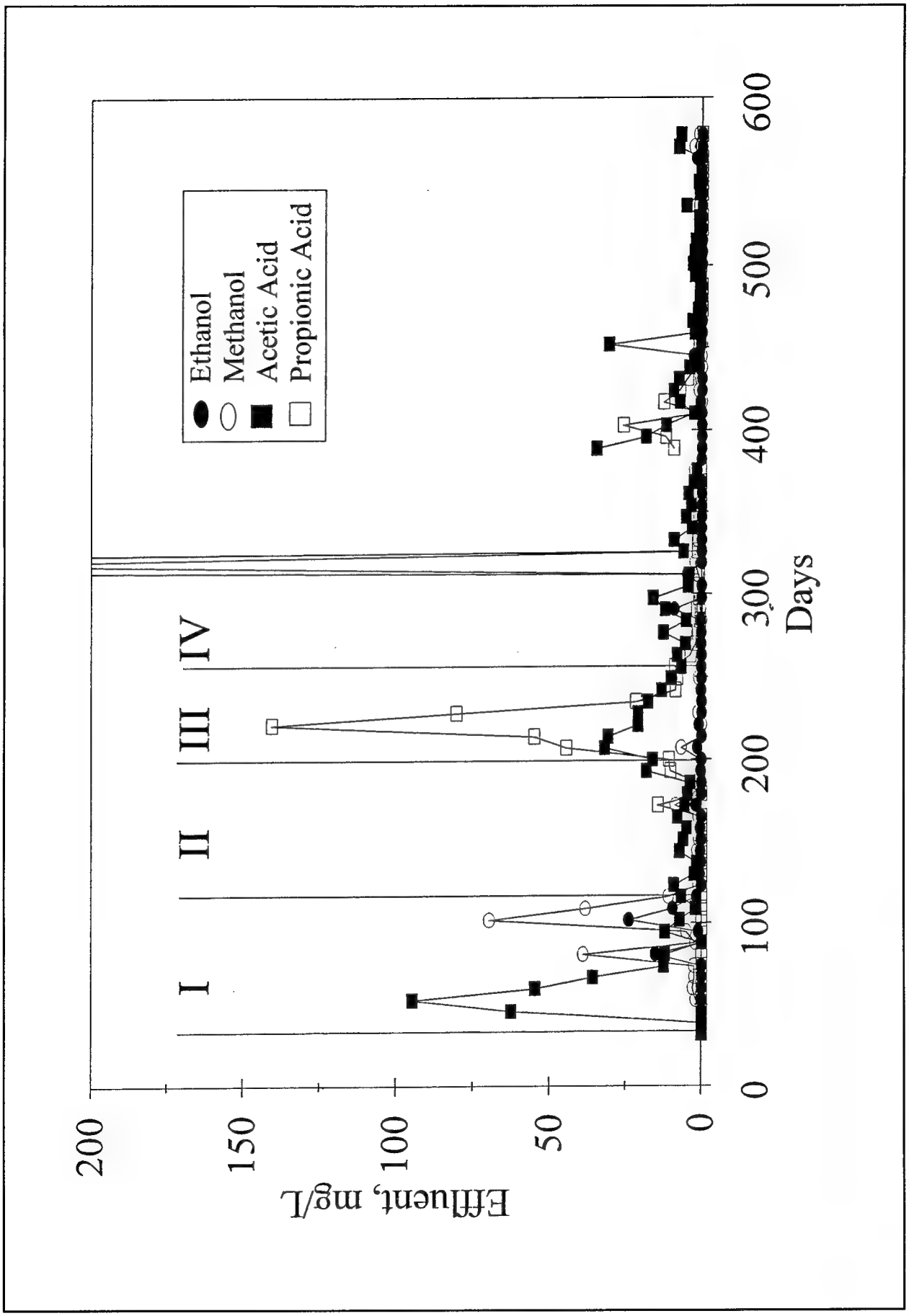

Figure 7. Volatile acids and alcohols—Column A.

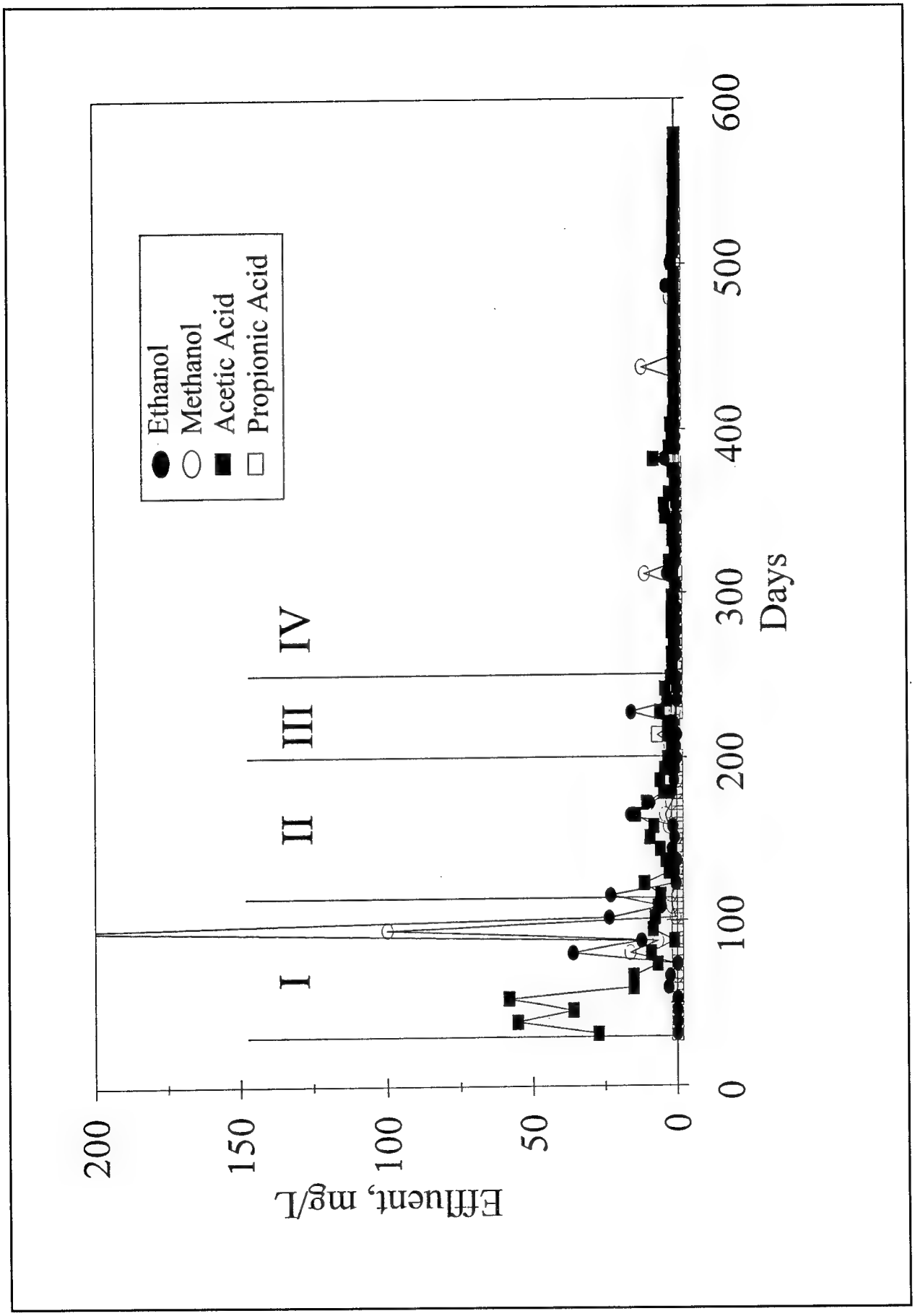

Figure 8. Volatile acids and alcohols—Column B.

Table 17. Effluent quality vs feed ethanol concentrations (Stage IV).

Feed Ethanol Conc.	Influent		Effluent						% COD Conversion	
	2,4-DNT mg/L	COD g/d	Ethanol mg/L	Methanol mg/L	Acetic Acid mg/L	Propionic Acid mg/L	2,4-DNT mg/L	COD g/d	to Methane	to Effluent
Column A										
6000 mg/L	110	57.79 (3.69)	0.41 (0.64)	0.61 (1.65)	6.35 (6.49)	2.98 (5.09)	0.028 (0.042)	1.46 (0.54)	92.4	2.53
2000 mg/L	110	30.42 (11.1)	0.47 (0.94)	0.31 (0.67)	3.02 (1.09)	0.20 (0.35)	ND	1.02 (0.08)	88.5	3.33
Column B										
600 mg/L	110	7.94 (1.19)	0.40 (1.05)	0.62 (2.30)	1.96 (1.56)	0.21 (0.40)	0.019 (0.035)	1.31 (0.58)	93.8	16.5
200 mg/L	110	2.88 (0.02)	0.35 (0.87)	0.91 (2.90)	0.69 (0.21)	ND	0.001 (0.016)	1.04 (0.12)	93.1	36.1
0 mg/L	110	0.33 (0.01)	ND	ND	0.36 (0.12)	ND	0.170 (0.300)	0.70 (0.05)	3.0	213.4*

Note: Standard Deviation represented in parenthesis.
*Indicates displacement of DAT by DNT in the absence of ethanol.

Table 18. Effluent concentrations of DNT and biotransformed products.

Ethanol Concentrations	2,4-DNT mg/L	2-A-4-NT mg/L	4-A-2-NT mg/L	2,4-DAT mg/L
Column A				
6000 mg/L	0.028 (0.042)	ND	0.084 (0.111)	80.02 (2.80)
2000 mg/L	ND	ND	0.224 (0.382)	75.02 (7.74)
Column B				
600 mg/L	0.019 (0.035)	NA	NA	NA
200 mg/L	0.001 (0.016)	ND	0.072 (0.210)	71.21 (3.87)
0 mg/L	0.170 (0.300)	0.103 (0.226)	0.234 (0.317)	55.61 (13.62)

Note: Standard deviation represented in parentheses.

Table 19. Contribution to effluent COD.

Ethanol Conc.	Alcohols & Acids g/d	2,4-DNT g/d	2-A-4-NT g/d	4-A-2-NT g/d	2,4-DAT g/d	Total COD Contribution to Effluent	Percent Eff. COD (2,4-DAT)	Percent Eff. COD (Total)
Column A								
6000 mg/L	0.0579	0.0001	0	0.0007	1.0707	1.1294	73.34	77.36
2000 mg/L	0.0202	0	0	0.0018	0.9903	1.0123	97.09	99.25
Column B								
600 mg/L	0.0188	0.0001	NA	NA	NA	NA	NA	NA
200 mg/L	0.0148	0	0	0.0006	0.9527	0.9681	91.61	93.09
0 mg/L	0.0011	0.0009	0.0008	0.0019	0.6905	0.6952	98.64	99.31

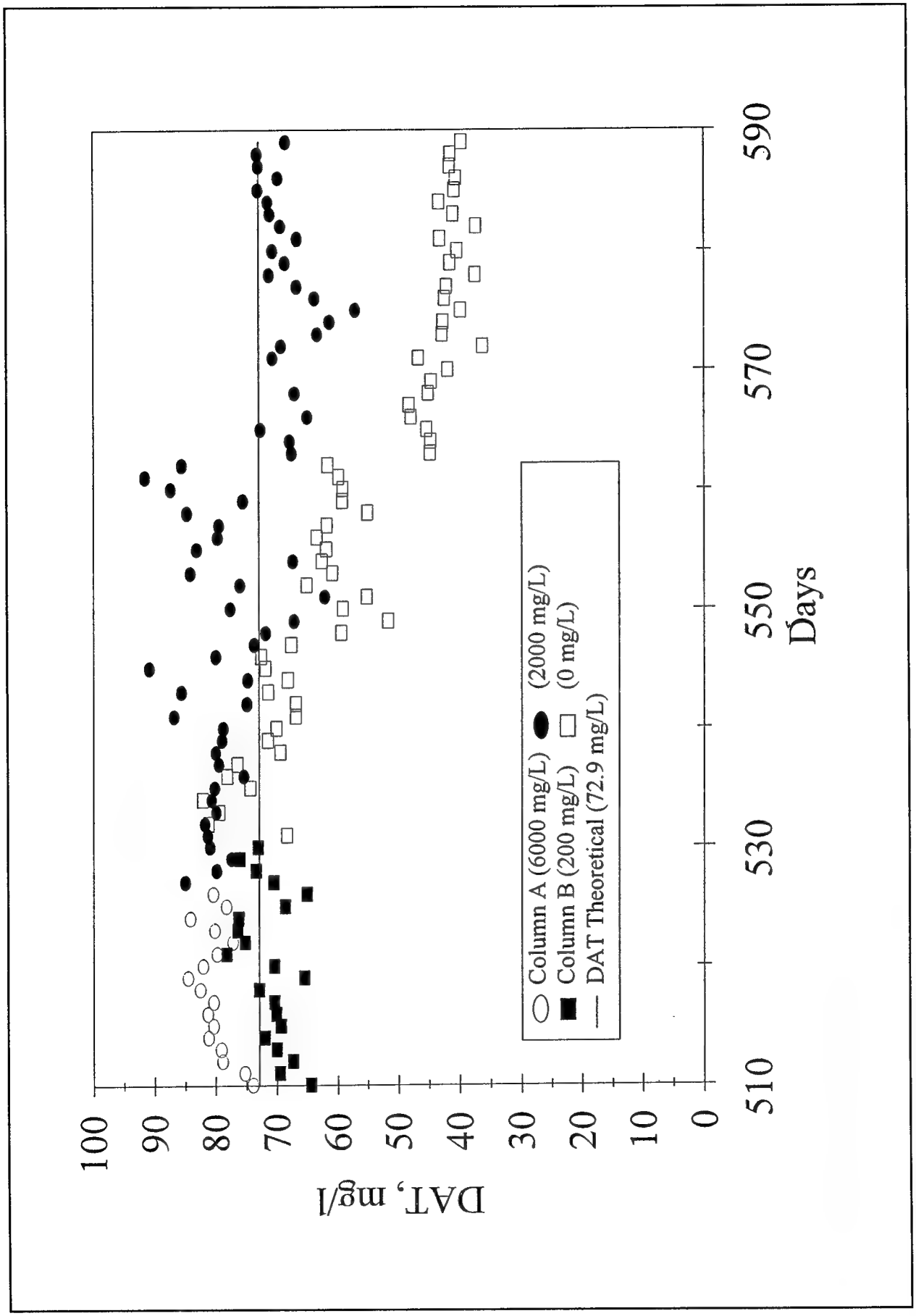

Figure 9. Effluent DAT concentrations for varying feed ethanol concentrations.

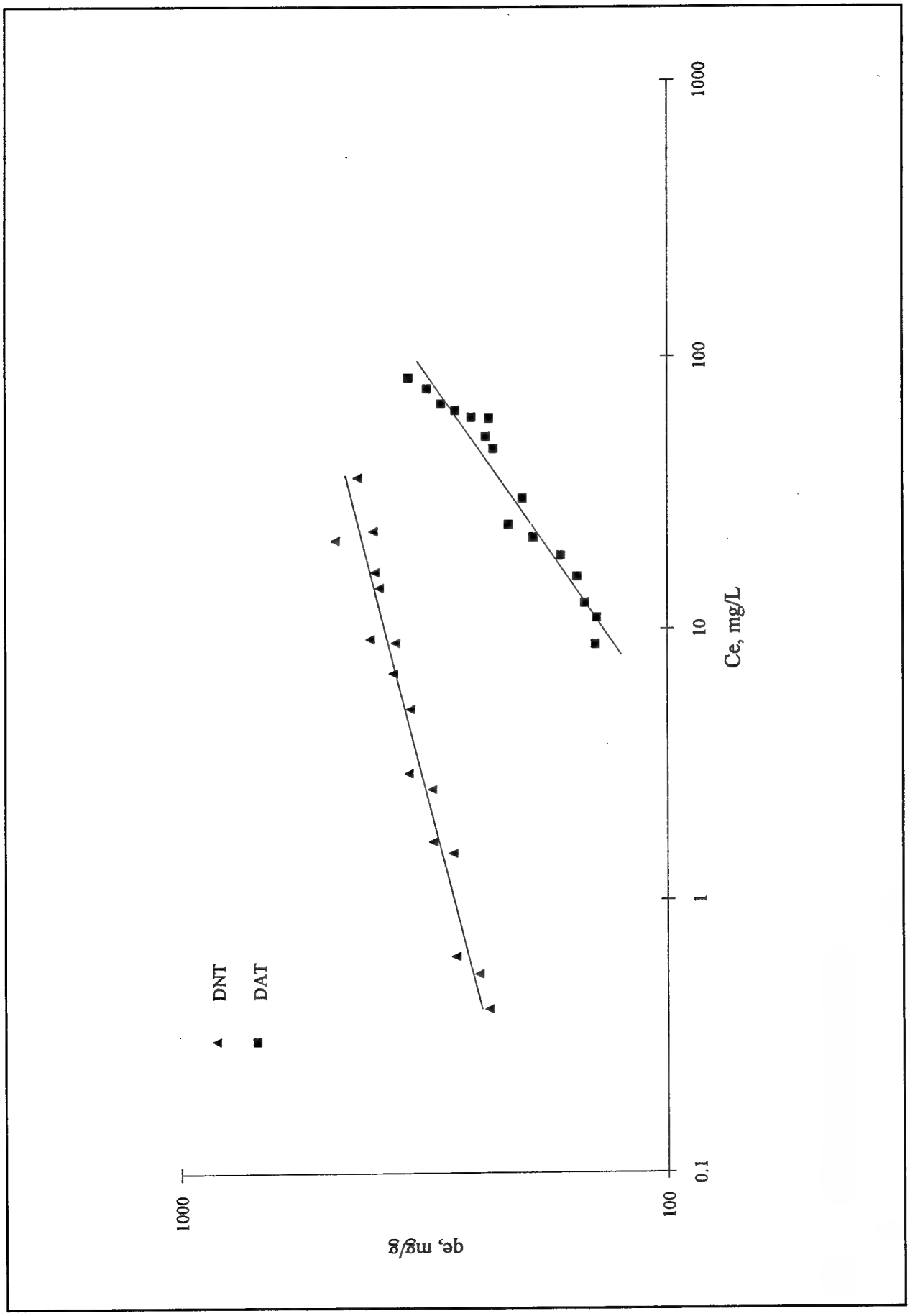

Figure 10. Anoxic adsorption isotherms for DNT and DAT.

Table 20. Effect of feed ethanol concentrations on retention of DNT and biotransformed products on GAC (mg of compound/gram GAC)

Ethanol Concentrations	Number of Samples	2,4-DNT	2-A-4-NT	4-A-2-NT	2,4-DAT
Column A					
6000 mg/L	10	0 (0)	6.6 (3.5)	12.3 (5.4)	60.3 (18.0)
2000 mg/L	5	0 (0)	1.8 (1.4)	2.7 (2.7)	19.2 (7.4)
Column B					
600 mg/L	7	0 (0)	4.8 (1.9)	5.0 (1.7)	51.8 (10.7)
200 mg/L	3	0 (0)	5.4 (2.9)	4.8 (2.0)	43.3 (8.1)
0 mg/L	5	5.9 (7.2)	9.9 (7.0)	5.4 (3.5)	17.9 (10.3)

Note: Standard deviation represented in parentheses.

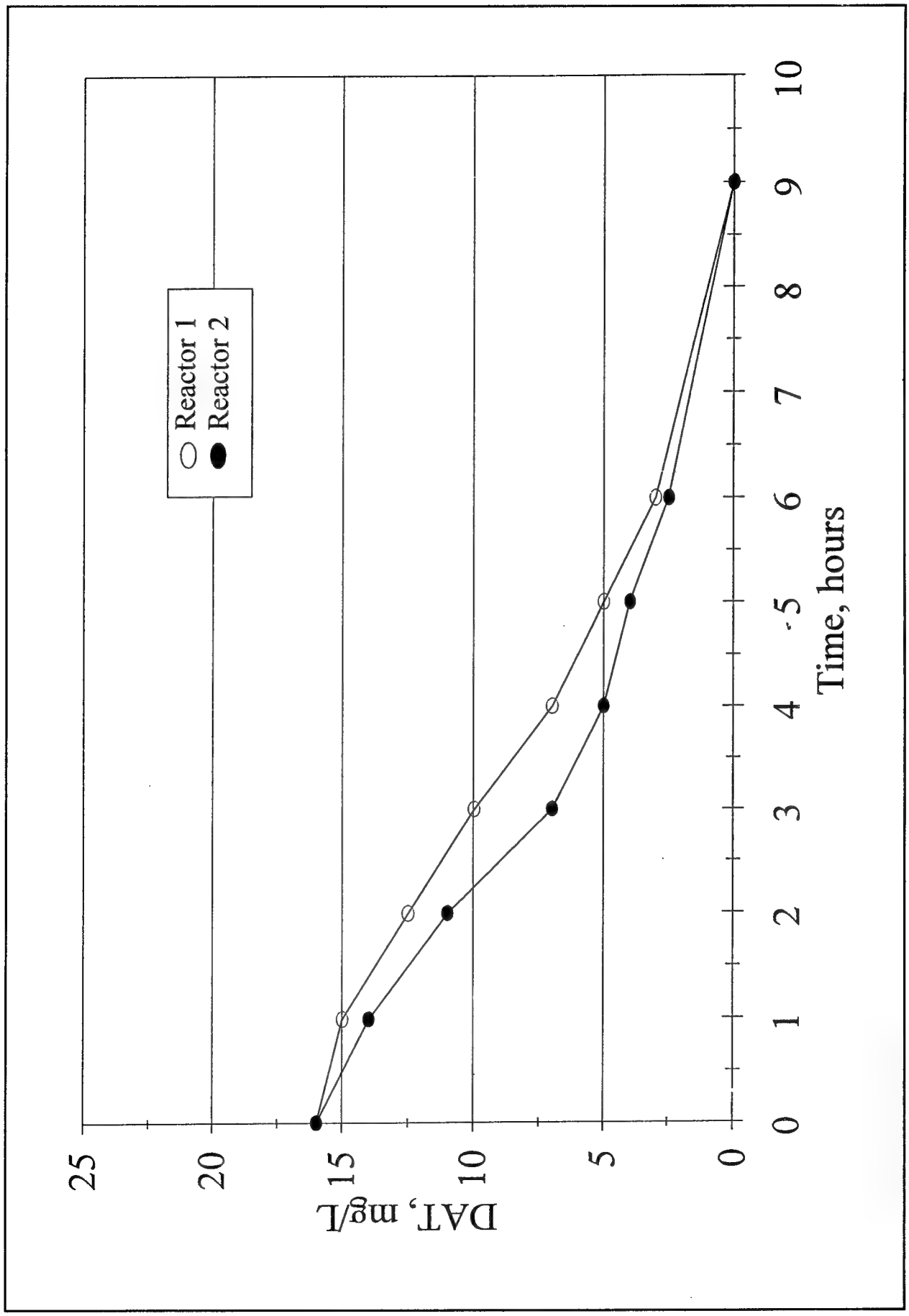

Figure 11. Activated sludge batch test.

Table 21. Batch-fed activated sludge reactor performance.

Days of Operation	Q, L/d		2,4-DAT mg/L	4-A-2-NT mg/L	2-A-4-NT mg/L	2,4-DNT mg/L
20 - 30	1.0	Influent	24.24 (4.00)	0 (0)	0 (0)	0 (0)
		Effluent #1	0.46 (1.53)	0 (0)	0 (0)	0 (0)
		Effluent #2	0 (0)	0 (0)	0 (0)	0 (0)
31 - 43	1.5	Influent	28.57 (2.93)	0.25 (0.38)	0 (0)	0 (0)
		Effluent #1	0.85 (1.99)	0.19 (0.33)	0 (0)	0 (0)
		Effluent #2	0.17 (0.29)	0.06 (0.18)	0 (0)	0 (0)
44 - 65	1.0	Influent	16.05 (1.70)	0.13 (0.16)	0.07 (0.12)	0.02 (0.07)
		Effluent #1	0.17 (0.46)	0.19 (0.28)	0.10 (0.24)	0 (0)
		Effluent #2	0.28 (0.48)	0.22 (0.31)	0.12 (0.25)	0 (0)

Note: Standard deviation is represented in parentheses.

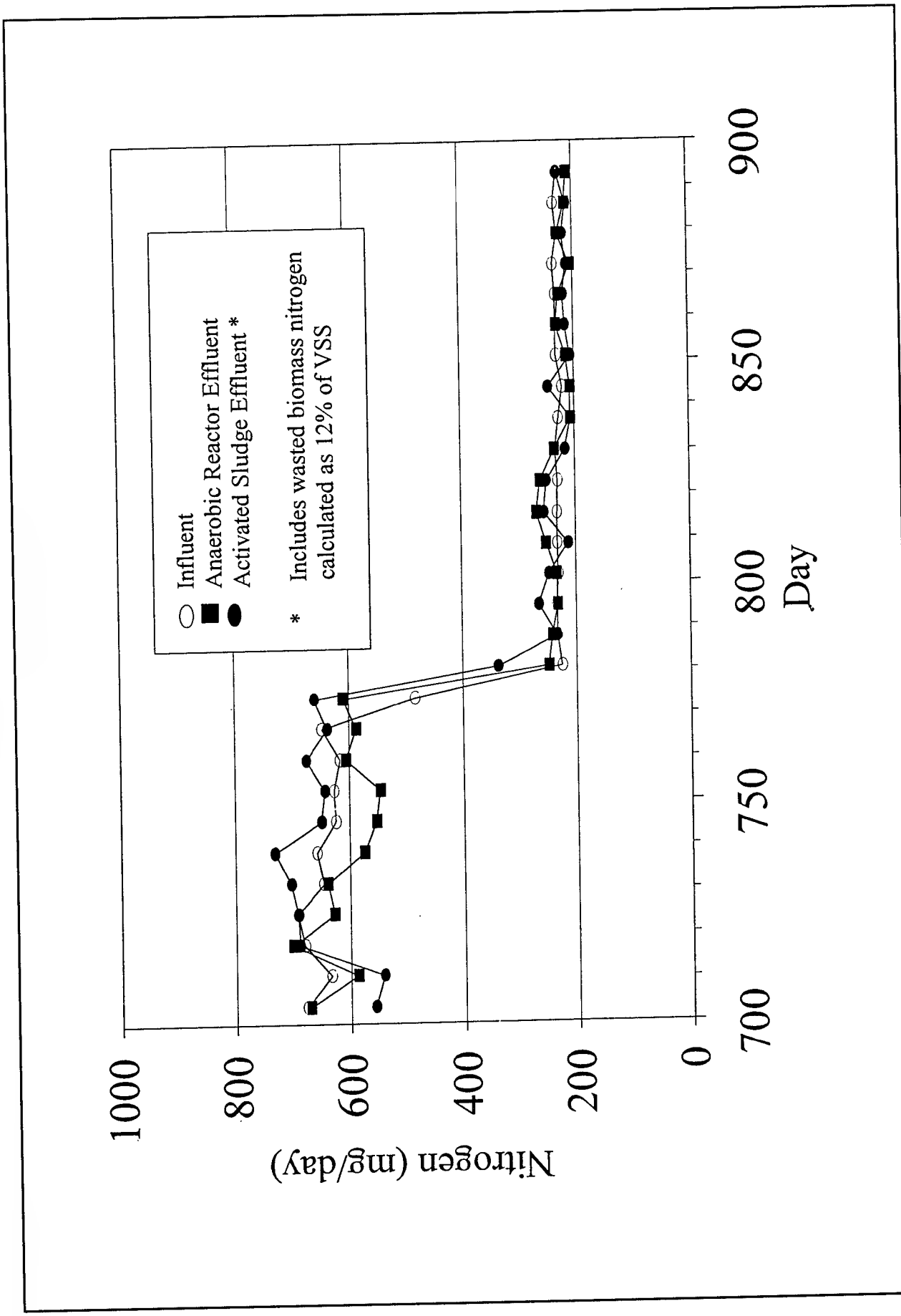

Figure 12. Continuous system nitrogen balance.

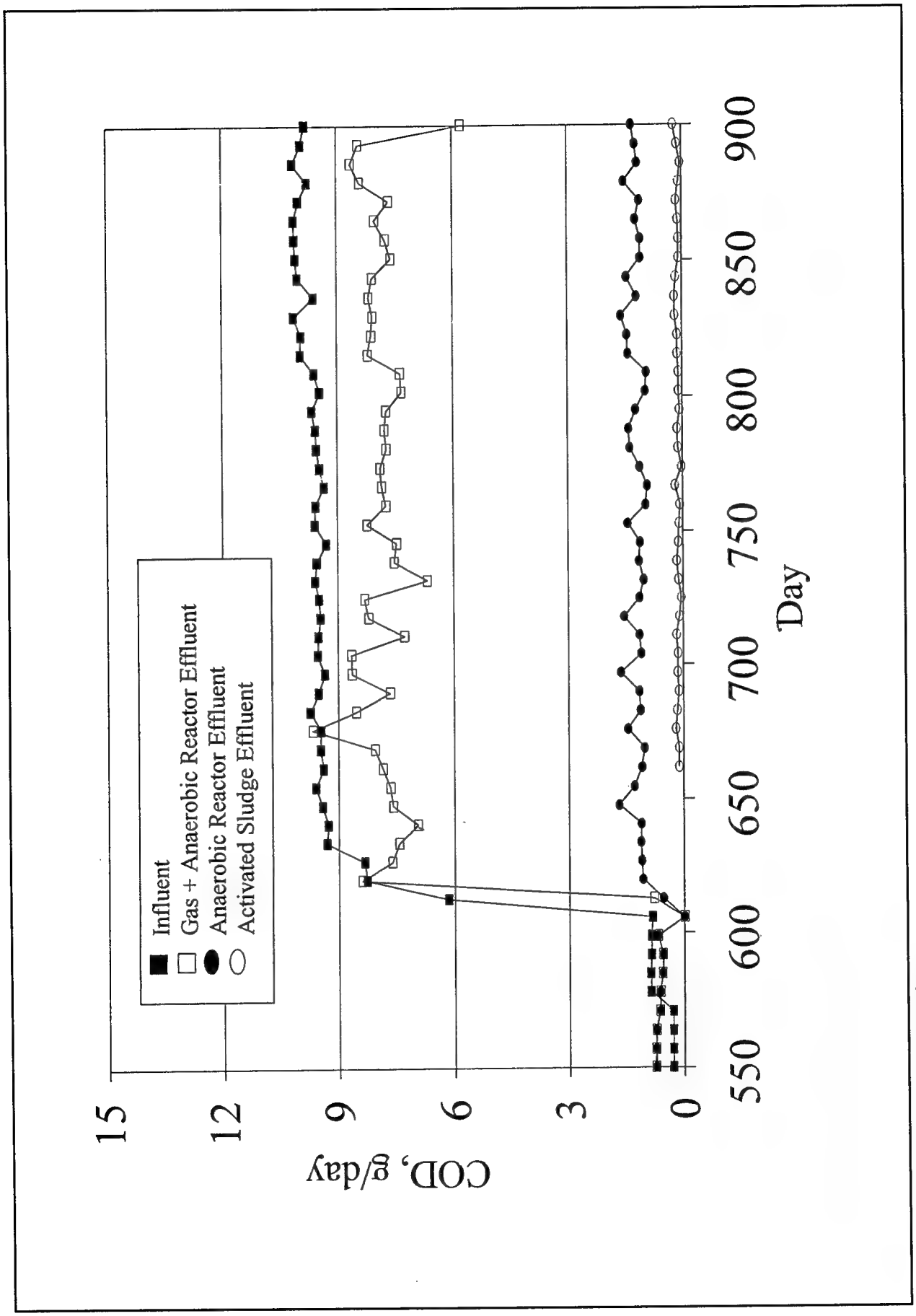

Figure 13. Continuous system COD balance.

Table 22. Influent and effluent organic concentrations.

	Influent				Effluent	
	DNT mg/L	Ether mg/L	Alcohol mg/L	COD mg/L	DNT mg/L	DAT mg/L
Average	142	377	2410	9200	1.04	82
Low	50	ND	60	1730	ND	13
High	208	2060	9212	27700	25.0	263
Standard Deviation	34	403	1844	4950	4.44	56

Table 23. Daily analysis log, Phase I.

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	GAC level, cm	Comments
1	9-15-92	3:35 p.m.	19.50		2.00		7.25	50135		35		107	Column start-up
2	9-16-92	1:55 p.m	4.65	5.21	1.00	1.07		50220	9.14	35		104	Initiated plant wastewater
	9-16-92	2:35 p.m.	19.50		8.00		7.45	50221		35		104	
	9-16-92	3:30 p.m.	12.80										
3	9-17-92	9:00 a.m.	9.00	5.21	7.17	1.04	7.08	50257	4.65	35		109	Added 0.5 Na2CO3/L
	9-17-92	2:30 p.m.	7.90		6.90		7.06	50261		36		109	Added 0.25 g/L Na2CO3
4	9-18-92	9:30 a.m.	3.65	5.24	6.00	1.15	7.02	50274	1.66	35		109	
	9-18-92	11:00 a.m.	21.00										Added 0.5 g Na2CO3/L
5	9-19-92	10:55 a.m.	16.00	5.00	4.95	0.99	6.93	50284	0.94	36	72	108	Added 5 mL EtOH added 1.0 g/L Na2CO3
6	9-20-92	5:20 p.m.	9.80	4.89	3.60	1.06	7.08	50304	1.58	36	70.5	109	
7	9-21-92	9:25 a.m.	6.75	4.55	3.00	0.9	7.09	50311	1.04	36	72	109	Have enough buffer solution to run all week
	9-21-92	9:40 a.m.	11.65		3.00		7.09	50311		36	72	109	
8	9-22-92	9:20 a.m	7.00	4.71	2.00	1.01	7.08	50323	1.22	36	70	107	Added 1mL EtOH
	9 22-92	1:35 p.m.	6.10		1.70		7.11	50325		36	75	107	
9	9-23-92	8:00 a.m.	2.50		0.95	1.17	6.96	50334		36	70	107	
	9-23-92	8:50 a.m.	2.10										
	9-23-92	8:55 a.m.	20.75	4.98	8.10	1.07	7.02	50334	1.12	36	70	107	Changed to new solutions
	9-23-92	2:30 p.m.	19.75		7.90		7.04	50338		36	74	107	
10	9-24-92	9:20 a.m.	16.00	4.67	7.25	0.84	7.18	50348	1.38	36	63	107	Pulled samples for lab

Table 23. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	GAC level, cm	Comments
	9-24-92	9:30 a.m.	18.00		8.00		7.18	50,348		36	63	107	Added buffer and nutrient to last through weekend
11	9-25-92	8:30 a.m.	13.80	4.35	7.25	0.78	7.33	50361	1.35	35.5	63.5	108	Added 1 mL HCl to buffer soln
12	9-26-92	4:25 p.m.	7.40	4.81	6.20	0.79	7.51	50379	1.35	36	68	107	Added 5 L of new buffer soln
	9-26-92	4:40 p.m.	12.40										
14	9-28-92	9:45 a.m.	4.55	4.45	4.90	0.74	7.1	50395	0.91	36	68	107	
	9-28-92	2:00 p.m.	3.35		4.70		7.2	50397		36	68	107	
14	9-28-92	2:00 p.m.	21.00		4.70		7.2	50397		36	68	107	Changed buffer soln
15	9-29-92	11:00 a.m.	17.00	4.94	4.05	0.81	7.09	50401	0.57	36	64	105	
16	9-30-92	7:45 a.m.	13.00	4.63	3.50	0.64	7.32	50403	0.23	35	64	107	Added 2 mL of HCl
	9-30-92	2:30 p.m.	11.75		3.30		7.3	50405		36	64	107	Added 3 mL of HCl
17	10-1-92	9:30 a.m.	8.10	4.57	2.80	0.65	7.18	50407	0.37	36	60	107	
	10-1-92	1:30 p.m.	7.40		2.18		7.2	50408		36	64	107	
	10-1-92	1:35 p.m.	21.00		8.00		7.2	50408		36	64	107	Changed buffer & nutrient
18	10-2-92	7:30 a.m.	17.70	4.36	7.55	1.17	7.24	50411	0.44	35	63	107	
19	10-3-92	7:30 p.m.	10.50	4.80	6.55	0.67	7.14	50416	0.33	36	66	107	
	10-3-92	7:40 p.m.	21.00		6.55		7.14	50416		36	66	107	Filled buffer to 21.00
21	10-5-92	9:30 a.m.	13.75	4.58	5.50	0.66	7.14	50422	0.38	36	63	107	
	10-5-92	9:40 a.m.	19.50		8.00		7.14	50422		36	63	107	Filled buffer and nutrient soln

Table 23. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	GAC level, cm	Comments
22	10-6-92	9:45 a.m.	15.00	5.69	7.45	0.54	7.14	50425	0.3	35	62	109	
23	10-7-92	10:30 a.m.	10.20	4.65	6.75	0.68	7.16	50428	0.29	35	62	107	
23	10-7-92	11:20 a.m.	9.90		6.70		7.16	50428		35	62	107	Sampled influent - 230 mL for CERL
24	10-8-92	10:00 a.m.	5.50	4.80	6.10	0.66	7.14	50434	0.61	35	60	107	
	10-8-92	2:00 p.m.	4.70		6.00		7.14	50435		36	74	107	
	10-8-92	2:15 p.m.	21.00		6.00		7.14	50435		36	74	107	Changed buffer soln
25	10-9-92	10:00 a.m.	17.00	4.80	5.40	0.7	7.06	50456	2.2	36	72	107	Added 8 gr. Na2CO3
26	10-10-92	9:30 a.m.	11.90	5.20	4.65	0.77	7.15	50480	2.45	36	70	107	
	10-10-92	9:50 a.m.	16.50		4.65		7.15	50480		36	70	107	Added buffer soln
28	10-12-92	9:30 a.m.	6.50	5.00	3.15	0.75	7.2	50518	1.9	36	70	107	
	10-12-92	10:00 a.m.	14.50		3.15		7.2	50518		36	70	107	Added buffer soln
	10-12-92	1:30 p.m.	13.50		3.00		7.22	50522		36	70	107	Pulled 300 mL for U. of Cincinnati
29	10-13-92	9:30 a.m.	9.50	5.00	2.25	0.9	7.17	50537	1.9	36	70	107	Strong odor of sulfide
30	10-14-92	9:00 a.m.	4.75	4.85	1.40	0.87	7.11	50556	1.94	36	70	109	
	10-14-92	2:30 p.m.	3.50		1.20		7.12	50561		36	73	109	
	10-14-92	2:45 p.m.	21.00		8.00		7.12	50561		36	73	109	Changed buffer and nutri-ents
31	10-15-92	10:00 a.m.	17.00	5.04	7.40	0.77	7.04	50580	2.3	36	70	109	Added 8 grams of Na2CO3
	10-15-92	1:00 p.m.	16.50		7.30		7.06	50583		36	70	109	

Table 23. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	GAC level, cm	Comments
	10-15-92	1:20 p.m.	19.50		7.30		7.06	50583		36	70	109	Added 3 L of buffer soln
32	10-16-92	1:40 p.m.	14.50	4.77	6.35	0.91	7.14	50606	2.26	36	72	109	
34	10-18-92	4:00 p.m.	4.00	5.00	4.50	0.88	7.18	50653	2.24	36	70	109	
	10-18-92	4:10 p.m.	8.00		5.50		7.18	50653		36	70	109	Added 1 L and 4 L of nutrient buffer
35	10-19-92	2:00 p.m.	3.55	4.08	4.75	0.69	7.14	50677	2.62	36	69	109	
	10-19-92	2:20 p.m.	21.00		4.75		7.14	50677		36	69	109	Changed to new buffer; water jacket leaking
36	10-20-92	10:00 a.m.	17.50	4.20	4.50	0.3	7.18	50703	3.12	36	65	109	Water jacket leaking badly
37	10-21-92	11:00 a.m.	13.00	4.32	3.70	0.77	7.12	50734	2.98	36	70	109	Leak fixed
	10-21-92	2:30 p.m.								36	69	107	Effluent sample No. 5
38	10-22-92	9:30 a.m.	8.75	4.53	3.00	0.75	7.12	50764	3.2	36	69	107	
	10-22-92	2:00 p.m.	8.00		2.85		7.11	50769		36	69	107	
38	10-22-92	2:15 p.m.	21.00		8.00		7.11	50769		36	70	107	Changed buffer and nutrients soln
	10-22-92	2:15 p.m.						50783					Calibrated gas meter
39	10-23-92	9:25 p.m.	17.50	4.25	7.55	0.6	7.15	50807	4.3	36	69	108	
40	10-24-92	9:25 p.m.	13.10	4.40	6.85	0.7	7.12	50838	3.1	36	69	108	
42	10-26-92	10:30 a.m.	4.00	4.46	5.35	0.73	7.02	50901	3.08	36	69	108	
	10-26-92	10:35 a.m.	19.50		8.00		7.02	50901		36	69	108	Changed buffer & nutrients; added 10 gr. Na2CO3
43	10-27-92	8:45 a.m.	15.40	4.42	7.35	0.7	7.19	50927	2.8	36	69	108	

Table 23. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	GAC level, cm	Comments
44	10-28-92	8:35 a.m.	11.00	4.43	6.65	0.7	7.4	50954	2.72	36	70	109	Added 7 mL HCl
	10-28-92	2:00 p.m.	10.00		6.50		7.4	50961		36	70	109	pH too high; changed over to new solution
	10-28-92	2:00 p.m.	21.00		6.50		7.4	50961		36	70	109	
45	10-29-92	11:00 a.m.	17.40	4.18	5.85	0.73	7.2	50983	2.63	36	70	109	
	10-29-92	11:10 a.m.	21.00		5.85		7.2	50983		36	70	109	Added buffer solution
46	10-30-92	10:00 a.m.	17.10	4.07	5.15	0.73	7.12	51006	2.4	36	70	109	
48	11-1-92	4:00 p.m.	7.50	4.27	3.20	0.87	7.12	51061	2.44	36	70	107	
49	11-2-92	9:50 a.m.	4.50		2.90		7.1	51079		36	70	107	
	11-2-92	2:30 p.m.	3.50	4.27	2.80	0.43	7.1	51084	2.45	36	70	107	Changed nutrient hose; changed buffer soln
	11-2-92	2:35 p.m.	21.00		2.80		7.1	51084		36	70	107	Changed buffer soln.
50	11-3-92	9:35 a.m.	17.80	4.04	2.30	0.63	7	51101	2.15	36	70	107	Added 10 g Na2CO3
51	11-4-92	9:45 a.m.	13.60	4.16	1.60	0.69	7.04	51123	2.18	36	68	107	Added 8 gr Na2CO3
52	11-5-92	9:45 a.m.	9.60	4.00	0.85	0.75	7.2	51145	2.2	36	72	107	
	11-5-92	10:00 a.m.	9.60		8.00		7.2	51145		36	72	107	Changed to new nutrient soln
	11-5-92	2:00 p.m.	8.90		7.90		7.2	51152		36	71	109	
	11-05-92	2:10 p.m.	21.00		7.90		7.2	51152		36	71	109	Changed to new buffer soln
53	11-06-92	9:30 a.m.	18.00	3.74	7.40	0.61	7.22	51159	1.42	36	71	107	
55	11-08-92	2:00 p.m.	9.00	4.11	5.85	0.71	7.1	51180	0.96	36	70	107	

Table 23. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	GAC level, cm	Comments
56	11-09-92	9:45 a.m.	6.00	3.64	5.25	0.72	7.08	51187	0.85	35	69	107	
57	11-10-92	10:00 a.m.	2.00	3.96	4.50	0.74	7.11	51195	0.79	36	70	107	
	11-10-92	10:10 a.m.	21.00		4.50		7.11	51195		36	70	107	Changed buffer soln
58	11-11-92	10:45 a.m.	17.00	3.88	3.75	0.73	7.2	51209	1.36	36	70	107	
59	11-12-92	11:00 a.m.	12.75	4.21	3.25	0.49	7.2	51226	1.68	36	70	107	Pulled sample *8
60	11-13-92	8:45 a.m.	7.00	6.34	2.40	0.94	7.2	51240	1.54	36	70	107	Pulled carbon sample
	11-13-92	1:00 p.m.	6.50		2.25		7.2	51243		36	70	107	
	11-13-92	1:15 p.m.	21.00		8.00		7.2	51243		36	70	107	Changed nutrient & buffer soln
62	11-15-92	3:00 p.m.	13.50	3.54	6.90	0.55	7.2	51268	1.24	36	70	107	
63	11-16-92	9:10 a.m.	10.00	4.60	5.85	1.38	7.08	51274	0.79	36	70	107	Added 8 grams Na2CO3
64	11-17-92	9:15 a.m.	6.00	4.00	5.10	0.75	7.12	51283	0.9	35	69	107	Added 5 mL/ethanol
65	11-18-92	8:45 a.m.	1.90	4.19	4.30	0.82	7.17	51319	3.68	35	70	107	
	11-18-92	9:20 a.m.	22.00		4.30		7.17	51321		35	70	107	Added 10 mL alcohol, changed buffer soln
66	11-19-92	8:50 a.m.	18.20	3.80	3.50	0.8	7.04	51335	1.6	35	70	107	Added 6.22 grams Na2CO3/18.2 liters buffer soln
	11-19-92	2:00 p.m.	17.40		3.35		7.05	51338		35	71.5	107	CERL & U of Cincinnati samples
	11-19-92	2:00 p.m.	16.80										After removal of 600 mL for samples
67	11-20-92	9:25 a.m.	13.40	4.65	2.70	0.78	7.32	51353	1.75	35	70	107	

Table 23. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	GAC level, cm	Comments
	11-20-92	9:45 a.m.	17.50		4.95								Added 2 grams/17.5 liters Na2CO3, added 2 mL EtOH
68	11-21-92	1:00 p.m.	12.30	4.54	3.80	1	7.28	51371	1.57	35	70	107	Added 1-1/2 mL HCl
70	11-23-92	9:00 a.m.	4.00	4.53	2.00	0.98	7.13	51398	1.47	35	70.5	107	
	11-23-92	9:25 a.m.	3.90		8.00			51398					New nutrient soln
	11-23-92	9:55 a.m.	3.80										New buffer soln. Added 10.5 grams Na2CO3, 1.04 grams sodium
	11-23-92	10:00 a.m.	21.00		8.00			51399		35	71	107	New solns
70	11-23-92	2:30 p.m.	20.10		7.80		7.11	51401		35	71	107	Added 0.5 grams Na2CO3/L
72	11-25-92	9:00 a.m.	15.80										Added remainder of previous soln
	11-25-92	9:00 a.m.	21.00										Added remainder of previous soln-added 6 grams Na2CO3, added
	11-25-92	1:45 p.m.	20.00		5.80		7.09	51422		35	70	107	
	11-25-92	2:30 p.m.	19.90		5.80			51422		35	70.5	107	Added 5 grams Na2CO3
74	11:28-92	2:55 p.m.	6.60	4.40	2.85	0.98	7.23	51457	1.1	35	65	107	
	11-28-92	3:10 p.m.	20.40		4.80			51457					Added remainder of nutrient soln, added 14L of soln; prepared
76	11-30-92	10:00 a.m.	12.60	4.35	3.05	0.98		51474	0.95	34	60	108	6.3 grams Na2CO3 (0.8 grams/L)

Table 23. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	GAC level, cm	Comments
77	12-01-92	10:00 a.m.	8.75	3.85	2.20	0.85	7.17	51484	1	34	60	108	
78	12-02-92	10:45 a.m.	4.60	4.02	1.30	0.87	7.2	51497	1.26	34	60	109	
79	12-03-92	9:30 a.m.	0.90	3.90	0.40	0.95	7.2	51506	0.95	35	70	107	Changed to new buffer and nutrient solution

Table 24. Daily analysis log, Phase II.

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	Gas level cm	Comments
1	12-31-92	1:15 p.m.	22.00		7.70		7.15	54297		34	66	109.2	Topped off buffer
4	01-03-93	10:30 a.m.	10.00		4.80		7.21	54641		34	62	111.8	
5	01-04-93	1:45 p.m.	5.40	4.05	3.70	0.97	7.20	54775	11.8	34	64	111.8	
	01-04-93	1:55 p.m.	22.00		8.80		7.20	54775		34	64	111.8	Topped off both solutions
8	01-07-93	10:00 a.m.	10.00	4.23	6.00	0.99	7.20	55011	8.3	34	70	109.2	
	01-07-93	10:15 a.m.	22.00		6.00		7.20	55011		34	70	109.2	Topped off buffer
12	01-11-93	10:15 a.m.	5.20	4.21	2.25	0.94	7.08	55484	11.8	34	72	111.8	
	01-11-93	10:30 a.m.	21.00		5.10			55486		34	72	111.8	25 gm Na2CO3 added to buffer
	01-11-93	3:30 p.m.	22.00		5.00			55540		34	72	111.8	Recal gas meter changed feed rate on both pumps
13	01-12-93	10:15 a.m.	16.00	4.68	3.85	1.25	6.80	55734	25	34	72	111.8	16 gm Na2CO3 added
	01-12-93	10:15 a.m.	18.30										Added old buffer soln
	01-12-93	10:30 a.m.											Added 5 pins to buffered soln
	01-12-93	11:00 a.m.											Pulled 250 mL for CERL sample
	01-12-93	11:15 a.m.	17.75		3.80			55745		34	72	109.2	
14	01-13-93	10:20 a.m.	9.80	8.50	2.50	1.35	7.02	56000	26.6	34	72	109.2	
	01-13-93	2:00 p.m.	8.65		2.30		7.04	56038		34	72	109.2	
14	01-13-93	2:10 p.m.	59.00		2.30		7.04	56038		34	72	109.2	Changed to big tank 59 L of buffer

Table 24. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	Gas level cm	Comments
15	01-14-93	10:30 a.m.	2.50	7.57	1.15	1.34	7.02	56241	23.8	34	72	109.2	
	01-14-93	10:40 a.m.	59.00		17.00		7.02	56241		34	72	109.2	Changed to larger nutrient tank and added buffer soln
	01-14-93	1:00 p.m.										109.2	Added 2 pins to nutrient timer
16	01-15-93	10:00 a.m.	51.50	7.66	15.90	1.12	7.11	56470	23.4	34	72	109.2	
	01-15-93	3:00 p.m.	49.90		15.50		7.11	56520		34	72	109.2	Four pins added to nutrient timer
19	01-18-93	9:00 a.m.	27.00	8.30	11.50	1.45	7.11	57193	24.48	33	71	111.8	Removed two pins from buffer soln. Pulled sampled #2.
20	01-19-93	9:00 a.m.	19.00	8.00	9.90	1.60	6.99	57430	23.7	33	71	127.0	Added 0.5 gm/L Na2CO3 to buffer. Removed 2 pins from buffered soln.
	01-19-93	9:35 a.m.	18.90		9.90			57435					
21	01-20-93	10:00 a.m.	11.00	7.68	8.50	1.34	7.18	57657	21.3	33	72	121.9	
	01-20-93	10:10 a.m.	55.00										New buffer added 1 gm/L Na2CO3 & 0.05 gm/L sodium sulfide
	01-20-93	11:00 a.m.	54.80		8.40			57664		33	72	110.5	
22	01-21-93	1:40 p.m.	46.30	7.69	6.80	1.45	6.82	57781	10.6	33	64	111.8	Added 23 gm Na2CO3
23	01-22-93	1:30 p.m.	38.80	7.58	5.40	1.41	7.00	57882	10.2	33	64	111.8	
	01-22-93	1:40 p.m.	57.40		21.50		7.00	57881		33	64	111.8	Filled nutrient & buffer solns

Table 24. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	Gas level cm	Comments
26	01-25-93	9:30 a.m..	36.40	7.41	18.90	0.92	7.30	58128	8.7	34	59	109.2	
27	01-26-93	9:30 a.m.	28.50	7.90	17.75	1.15	7.30	58222	9.4	34	70	109.2	
28	01-27-93	2:00 p.m.	19.90	7.24	16.75	0.84	7.31	58328	8.9	33	74	106.7	
29	01-28-93	10:00 a.m.	18.30	1.92	15.90	2.22	7.30	58405	9.2	33	71	101.6	Adjusted carbon level
30	01-29-93	9:00 a.m.	6.50	12.31	14.30	1.67	9.22	58418	1.4	34	72	81.3	Added 5 mL HCl directly to column
	01-29-93	9:20 a.m.	57.10				6.72	58419					Bottom column pH 7.33; added 3.15 gm sodium sulfide.
	01-29-93	10:00 a.m.	57.00		14.25		7.05	58433		34	72	99.1	Added 5 gm Na2CO3
	01-29-93	10:40 a.m.	56.90		14.20		7.15	58438		34	73	94.0	
	01-29-93	3:15 p.m.	55.50		13.90		7.32	58444		34	72.5	91.4	Adjusted fluidization
	01-29-93	4:15 p.m.	55.00		13.90			58463				101.6	
32	01-31-93	8:00 a.m.	43.00	7.20	11.60	1.38	6.86	58700	14.4	33	72	88.9	0.25 gm/L Na2CO3 added; adjusted fluidization
	01-31-93	10:00 a.m.	42.40		11.40			58728		33	72		GAC level not visible
	01-31-93	10:20 a.m.						58734				109.2	
33	02-01-93	10:30 a.m.	35.00	7.24	10.00	1.45	7.10	58776	6.9	33	72	99.1	
34	02-02-93	9:15 a.m.	28.00	7.38	8.80	1.27	7.93	58835	6.2	33	72	96.5	Added new buffered soln but no Na2CO3
	02-02-93	9:20 a.m.	46.80		8.80		7.93	58835		33	72	96.5	
35	02-03-93	9:30 a.m.	38.80	7.92	7.20	1.58	7.18	58846	1.1	33	70	99.1	Adjusted carbon level

Table 24. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	Gas level cm	Comments
	02-03-93	2:00 p.m.	37.50		7.00		7.19	58905		33	71	99.1	
36	02-04-93	10:30 a.m.	30.80	7.68	5.50	1.63	6.90	59047	19.3	33	72	99.1	
	02-04-93	11:00 a.m.	59.00		21.50		6.90	59048		33	72	99.1	Filled buffer & vitamin soln. 30 gm Na2CO3 added
37	02-05-93	10:00 a.m.	46.80	12.46	20.20	1.34	6.71	59207	16.2	33	71	97.8	12 gm Na2CO3 added
40	02-08-93	10:00 a.m.	30.00	5.60	15.60	1.53	6.10	59391	6.1	33	72	86.4	15 gm of Na2CO3 added
	02-08-93	1:30 p.m.					5.95	59395					No level (GAC), flushed circulating lines
	02-08-93	2:00 p.m.	28.40		15.20		6.35	59396					No GAC level
	02-08-93	3:00 p.m.	27.90		15.20		7.90	59397		33	74	91.4	
41	02-09-93	9:00 a.m.	21.60	8.76	14.00	1.67	5.20	59457	6.6	32	71		GAC appears to be at top. Added 10 gm Na2CO3 to top of column
	02-09-93	9:45 a.m.	21.00		13.90		7.90	59459					Broke up carbon
41	02-09-93	1:40 p.m.	19.80		13.70		7.05	59469		32	72		
	02-09-93	2:15 p.m.	19.50		13.60		7.00	59470					GAC level approx. 37 inches but cannot see through column
42	02-10-93	8:30 a.m.	13.00	8.78	12.40	1.63	5.21	59544	8.9	32	71.5	86.4	
	02-10-93	9:00 a.m.	54.00										Added 60 gm Na2CO3 to new buffer, 10 gm to top of column

Table 24. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	Gas level cm	Comments
	02-10-93	9:30 a.m.	53.70		12.30		8.97	59546		32	72		
	02-10-93	10:00 a.m.	53.50		12.30		8.72	59546					(Top left off) no gas
	02-10-93	2:45 p.m.	46.70		12.00		5.60	59570		33	74		Added 20 gm Na2CO3 to buffer soln, 10 gm Na2CO3 to column
	02-10-93	3:15 p.m.	46.60		11.90		8.72	59571		33	74	86.4	
43	02-11-93	7:30 a.m.	45.60	8.76	11.00	1.46	5.42	59640	10	32	72.5	86.4	Added 10 gm Na2CO3 to top of column
	02-11-93	11:45 a.m.	43.60		10.70		6.4	59663		32	73	86.4	Added 5 gm Na2CO3 to top of column
	02-11-93	12:30 p.m.	43.10		10.60		8.19	59667		32	73		
	02-11-93	1:35 p.m.	42.90		10.60		6.98	59673				81.3	Added 23 gm Na2CO3 to buffered soln
	02-11-93	2:00 p.m.											Pulled approx. 500 mL of carbon
43	02-11-93	2:50 p.m.	42.40		10.50		6.48	59678		32	73		Added 20 gm NaOH to buffer soln
44	02-12-93	7:50 a.m.	36.20	9.40	9.50	1.50	5.50	59752	11.2	34	72		
	02-12-93	7:50 a.m.	35.60										Pulled 500 mL of influent
	02-12-93	1:30 p.m.	33.70		9.10		5.63	59777		33	72.5	76.2	pH-bottom 6.02
	02-12-93	2:30 p.m.	33.30		8.90		5.58	59781		33	74		

Table 24. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	Gas level cm	Comments
	02-12-93	2:45 p.m.											Added 7.9 gm NaOH to buffer soln Removed 26 pins from buffer Removed 31 pins from nutrient to back down flow
	02-12-93	3:30 p.m.	33.20	5.42	8.90		5.65	59785		34	70		
45	02-13-93	9:00 a.m.	30.50	5.42	8.40	1.04	5.72	59819	6.7	34	73		Added 6 gm Na_2CO_3 to column. Added pins to buffer & nutrient.
46	02-14-93	7:30 a.m.	25.20	5.65	7.00	1.49	9.55	59832	1.4	34	72		Pulled pins to buffer and nutrient timers. Added carbon pulled on 2/11/93.
47	02-15-93	9:35 a.m.	19.70	5.08	5.75	1.56	6.01	59957	11.5	34	72		
	02-15-93	11.15 a.m.	19.00		5.70		6.01	59963					Added 1 mL 10 M NaOH to column
47	02-15-93	3:00 p.m.	18.30		5.50		6.09	59978		34	73		Added 2 mL 10 M NaOH to column. Added 4.3 g NaOH to buffer
48	02-16-93	8:25 a.m.	14.70	5.22	4.75	1.04	8.85	60017	6.3	34	72		
	02-16-93	4:05 p.m.	13.00		4.30		6.82	60030		34	72		
49	02-17-93	9:30 a.m.	9.00	5.47	3.50	1.20	9.45	60070	5.1	34	72		
	02-17-93	10:00 a.m.	8.90										
	02-17-93	10:10 a.m.	59.00										New buffer soln. Pulled 200 mL for lab

Table 24. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	Gas level cm	Comments
	02-17-93	3:40 p.m.	6.00		3.25		7.28	60073		34			Lower pH buffer soln to see if column will stabilize (see logbook)
50	02-18-93	8:00 a.m.	2.60	5.02	2.50	1.07	8.30	60084	1.5	34	70		
	02-18-93	3:10 p.m.	8.00		10.50		6.49	60087		34	73		Column re-startup
51	02-19-93	9:00 a.m.	3.80	5.60	9.50	1.33	5.46	60097	1.3	34	73	27.9	
	02-19-93	9:00 a.m.	53.00										Added 10 mL NaOH (10 M) to column. Changed to higher pH buffer
	02-19-93	11:45 a.m.	52.50		9.50		6.80	60101		34	73	40.6	Added 15 mL NaOH to column. Added 12.5 g NaOH to buffer
53	02-21-93	9:15 a.m.	40.80	6.07	7.10	1.19	7.40	60178	4	34	72	43.2	
53	02-21-93	10:15 a.m.	40.60		7.00		7.29	60180		34	72	43.2	Difficult to standardize pH meter
	02-21-93	6:30 p.m.					7.10			34	72	43.2	Adjusted carbon level
54	02-22-93	9:30 a.m.	35.00	5.74	6.00	1.09	7.48	60222	4.4	34	72	66.0	
55	02-23-93	9:30 a.m.	29.50	5.50	4.80	1.20	7.70	60265	4.3	34	72	66.0	pH high
	02-23-93	9:30 a.m.	43.00		4.80		7.70	60265		34	72	66.0	Filled buffer tank
56	02-24-93	9:30 a.m.	37.80	5.20	3.50	1.30	7.38	60302	3.7	34	72	66.0	
57	02-25-93	9:00 a.m.	32.40	5.51	2.40	1.12	7.10	60337	3.6	34	72	66.0	Added 15 gm Na2CO3
58	02-26-93	10:00 a.m.	26.40	5.76	1.20	1.15	6.84	60390	5.1	34	72	66.0	OK - pH a little low

Table 24. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	Gas level cm	Comments
	02-26-93	10:20 a.m.	58.40		9.40		6.84	60390		34	72	66.0	Filled solns/added 32 gram Na2CO3
61	03-01-93	9:30 a.m.	41.70	5.61	6.00	1.14	6.90	60610	7.4	34	72	66.0	Added 20 gram NaOH
62	03-02-93	1:00 p.m.	35.20	5.67	4.50	1.31	7.65	60725	10	34	72	66.0	pH-high
	03-02-93	1:15 p.m.	57.20		4.50		7.65	60725		34	72	66.0	Added more buffer for pH control
63	03-03-93	10:00 a.m.	52.80	5.03	3.70	0.91	7.98	60798	8.3	34	72	66.0	Added 18 mL HCL
64	03-04-93	9:15 a.m.	47.30	5.56	2.90	0.81	7.50	60876	7.9	34	74	68.6	
65	03-05-93	10:00 a.m.	41.30	5.82	2.00	0.87	7.20	60973	9.4	34	74	71.1	
	03-05-93	10:10 a.m.	41.30		10.00		7.20	60973		34	74	71.1	Filled nutrient soln
68	03-08-93	9:00 a.m.	25.20	5.44	7.50	0.84	7.28	61347	12.6	34	74	71.1	
69	03-09-93	8:30 a.m.	20.50	4.80	6.70	0.82	7.30	61456	11.3	34	74	71.1	
70	03-10-93	10:30 a.m.	15.30	4.80	5.90	0.74	7.28	61575	11	34	74	71.1	
	03-10-93	10:50 a.m.	39.00		13.90		7.28	61575		34	74	71.1	Added buffer & nutrients
71	03-11-93	10:50 a.m.	38.10	0.89	13.60	0.30	7.46	61598	2.3	27	64	96.5	Power was off this morning
72	03-12-93	9:00 a.m.	33.70	4.75	12.90	0.76	7.08	61697	10.7	34	64	86.4	
	03-12-93	2:30 p.m.	32.50		12.80		7.10	61723		34	68	76.2	Adjusted GAC level
75	03-15-93	8:45 a.m.	15.90	5.95	10.50	0.80	7.25	62084	12.9	32	60	81.3	
	03-15-93	9:00 a.m.	45.90		10.50		7.25	62084		32	60	81.3	Added buffer + 25 gr Na2CO3

Table 24. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	Gas level cm	Comments
76	03-16-93	9:00 a.m.	39.90	6.94	9.60	0.89	7.02	62296	21	33	70	81.3	Added 15 grams Na2CO3
77	03-17-93	9:30 a.m.	32.70	7.05	8.50	1.08	7.21	62545	24.4	33	71.5	81.3	
78	03-18-93	9:00 a.m.	26.10	6.74	7.20	1.33	7.24	62798	25.8	33	71	86.4	
	03-18-93	9:15 a.m.	59.00		7.20		7.24	62798		33	71	86.4	Added buffer/30 grams Na2CO3
79	03-19-93	9:45 a.m.	52.50	6.30	5.90	1.26	7.10	63047	24.1	33	70	86.4	
82	03-22-93	8:45 a.m.	32.70	6.69	2.00	1.32	7.09	63770	24.4	33	71	95.3	
	03-22-93	10:30 a.m.	32.00		1.90		7.11	63785		33	71	88.9	
	03-22-93	10:45 a.m.	59.00		17.90		7.11	63787		33	71	88.9	Added buffer & nutrients
83	03-23-93	9:40 a.m.	51.80		16.80		7.35	64057		34	71	88.9	Added 12 mL HCL to buffer
	03-23-93	9:45 a.m.	51.80	7.58	16.80	1.15	7.35	64078	29.6	34	71	88.9	Calibrated gas meter
84	03-24-93	10:15 a.m.	43.00	8.62	15.30	1.47	7.35	64357	27.3	33	72	91.4	
85	03-25-93	8:45 a.m.	35.20		13.80		7.36	64611		33	73	91.4	
	03-25-93	9:30 a.m.	55.00	8.05	13.80	1.55		64620	27.1				Added 20 liters buffered soln/took sample No. 23 Added 1.25 grams/liter Na2CO3 Added 0.05 grams/liter sodium sulfide
86	03-26-93	8:45 a.m.	46.90	8.36	12.30	1.55	7.28	64895	28.4	33	72.5	94.0	Removed 2 pins from buffered soln

Table 24. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	Gas level cm	Comments
89	03-29-93	9:45 a.m.	22.70	7.96	7.80	1.48	7.17	65735	27.6	34	72	101.6	Removed 2 pins from buffered soln
	03-29-93	10:00 a.m.	47.30										Added buffered soln 42 grams Na2CO3
90	03-30-93	9:30 a.m.	39.90	7.48	6.50	1.31	7.14	66019	28.7	33	72	91.4	
	03-30-93	1:30 p.m.											Power off
91	03-31-93	8:00 a.m.											Column shutdown; severly plugged
	03-31-93	9:30 a.m.	32.50	7.40	5.40	1.10	7.30	66085	6.6	33	70		Column operational
	03-31-93	2:00 p.m.	31.00		5.40		7.25	66102		33	70		Added 22 gr Na2CO3
91	03-31-93	2:10 p.m.	47.80		13.40		7.25	66102		33	70		Added buffer and nutrients
92	04-01-93	9:15 a.m.	41.20	8.19	12.20	1.21	5.97	66234	15.1	34	72.5		Pulled sample #25; added 41 gms Na2CO3
	04-01-93	10:15 a.m.	40.90		12.20		6.02	66239					
	04-01-93	2:00 p.m.	39.80		12.00		6.21	66261		34	73		
	04-01-93	3:00 p.m.	39.60		11.90		6.27	66268					
93	04-02-93	8:30 a.m.	33.70	6.47	11.00	1.21	7.23	66421	19.3	34	72.5	30.5	Sample of effluent; increased fluidization;
	04-02-93	9:00 a.m.	55.00		11.00		7.31	66425				40.6	Added 21.3 L buffered soln; added 1.05 gms sodium sulfide
	04-02-93	1:15 p.m.	53.90		10.80		7.39	60464		34	72.5	40.6	

Table 24. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	Gas level cm	Comments
95	04-05-93	8:15 p.m.	32.20	7.68	7.20	1.28	7.23	66786	12.2	34	72	40.6	Increased bed level
	04-05-93	8:45 a.m.										66.0	
96	04-06-93	9:20 a.m.	24.00	7.87	6.00	1.15	7.21	66905	11.4	34	72	63.5	
97	04-07-93	9:30 a.m.	16.50	7.42	4.90	1.09	7.20	67014	10.8	34	72	63.5	
	04-07-93	9:40 a.m.	48.50		4.90		7.20	67014		34	72	63.5	Added 1.5 gms sodium sulfate; added 48 gms Na2CO3; added buffer
98	04-08-93	10:10 a.m.	40.00	8.24	3.20	1.65	7.18	67077	6.1	34	72	94.0	
98	04-08-93	10:25 a.m.	59.00		11.20		7.18	67078		34	72	94.0	Topped off buffer and nutrients; no additions
102	04-12-93	10:00 a.m.	28.00	7.77	5.50	1.43	6.98	68451	34.4	34	73	91.4	
	04-12-93	10:20 a.m.	59.00		5.50		6.98	68454		34	73	91.4	Added 46 gms Na2CO3; added 1.50 gms sodium sulfide; topped off buffer
103	04-13-93	10:30 a.m.	51.00	7.84	4.00	1.47	5.57	68599	14.5	34	73	99.1	Added 60 gms Na2CO3
	04-13-93	1:30 p.m.	49.70		3.90		5.81	68610		34	73	99.1	Diluted buffer (see logbook)
	04-13-93	1:45 P.M.	59.00		3.90		5.81	68611		34	73	99.1	
104	04-14-93	9:30 a.m.	52.70	7.93	2.80	1.25	5.50	68649	5.2	34	73	96.5	Added 52 gms Na2CO3
105	04-15-93	9:30 a.m.	43.90	8.80	1.50	1.30	5.85	68721	7.2	34	73	96.5	
	04-15-93	9:40 a.m.	43.90		9.50		5.85	68721		34	73	96.5	Added nutrients

Table 24. (Cont'd).

Day	Date	Time	Vol., L	Q, L/d	Vol., L	Q, L/d	pH	Gas meter reading	Gas production L/d	Water Bath temp °C	Air temp °F	Gas level cm	Comments
106	04-16-93	9:00 a.m.	36.00	8.07	8.30	1.23	6.82	68798	7.9	34	74	94.0	

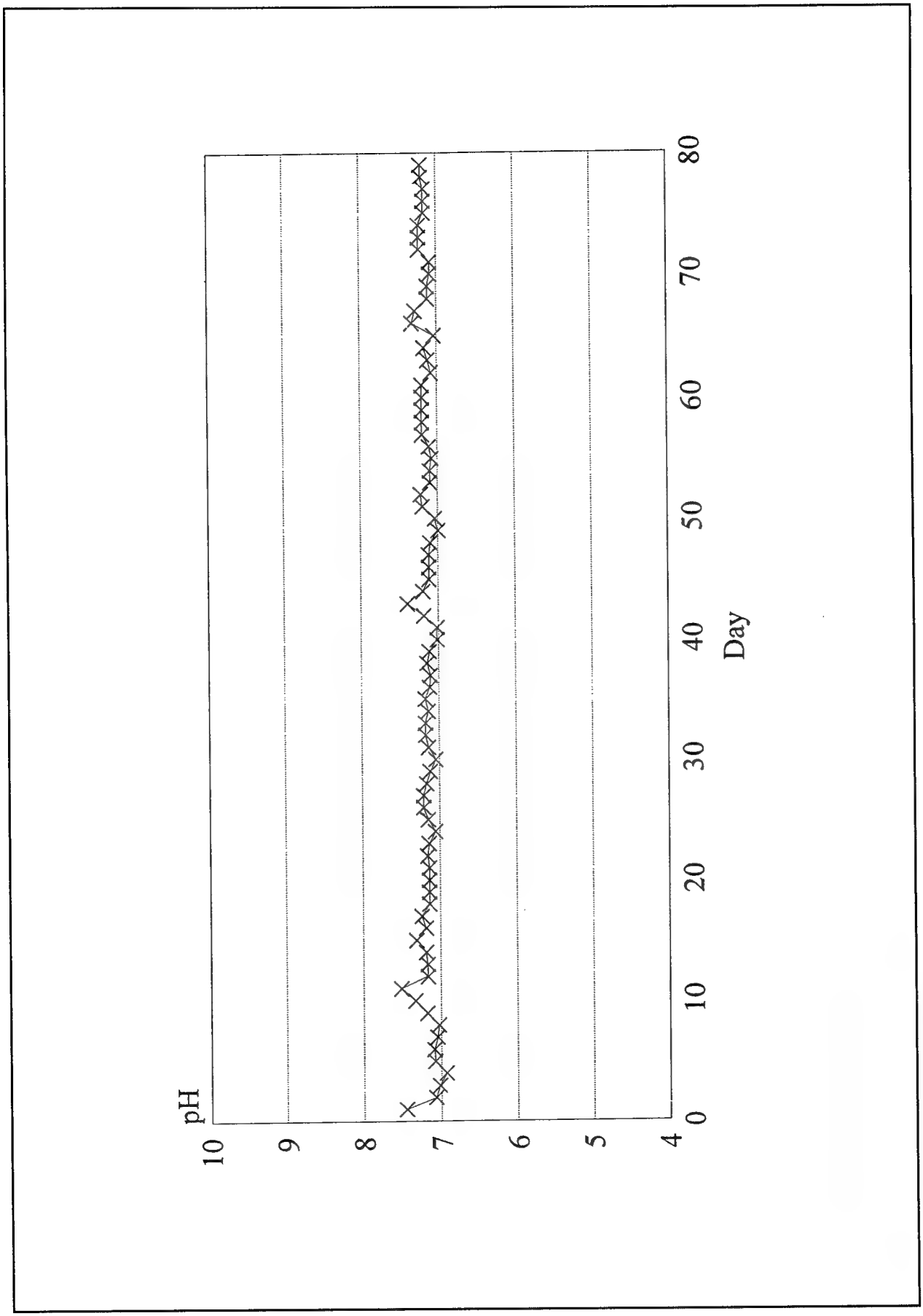

Figure 14. Measurement of pH, Phase I.

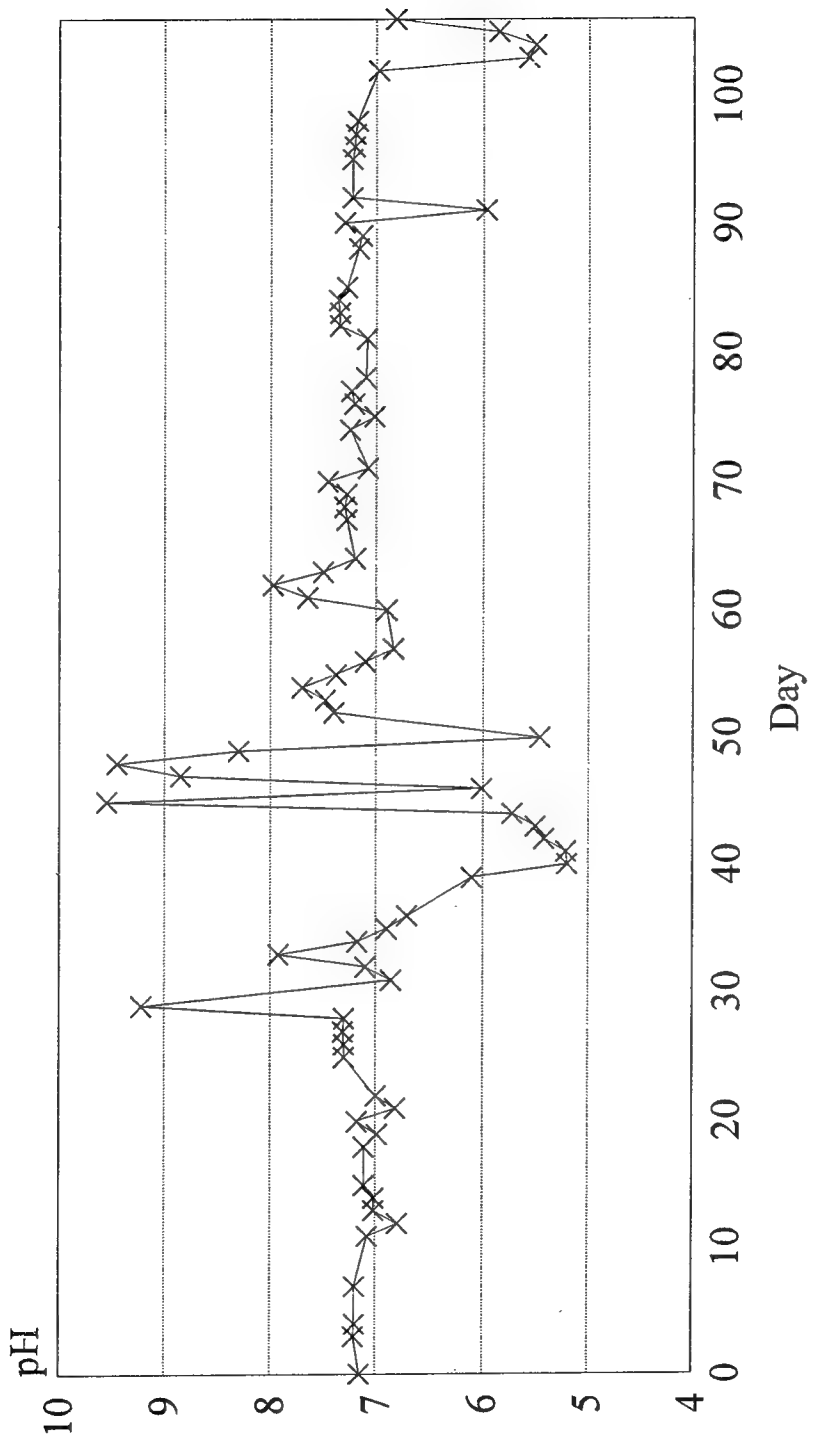

Figure 15. Measurement of pH, Phase II.

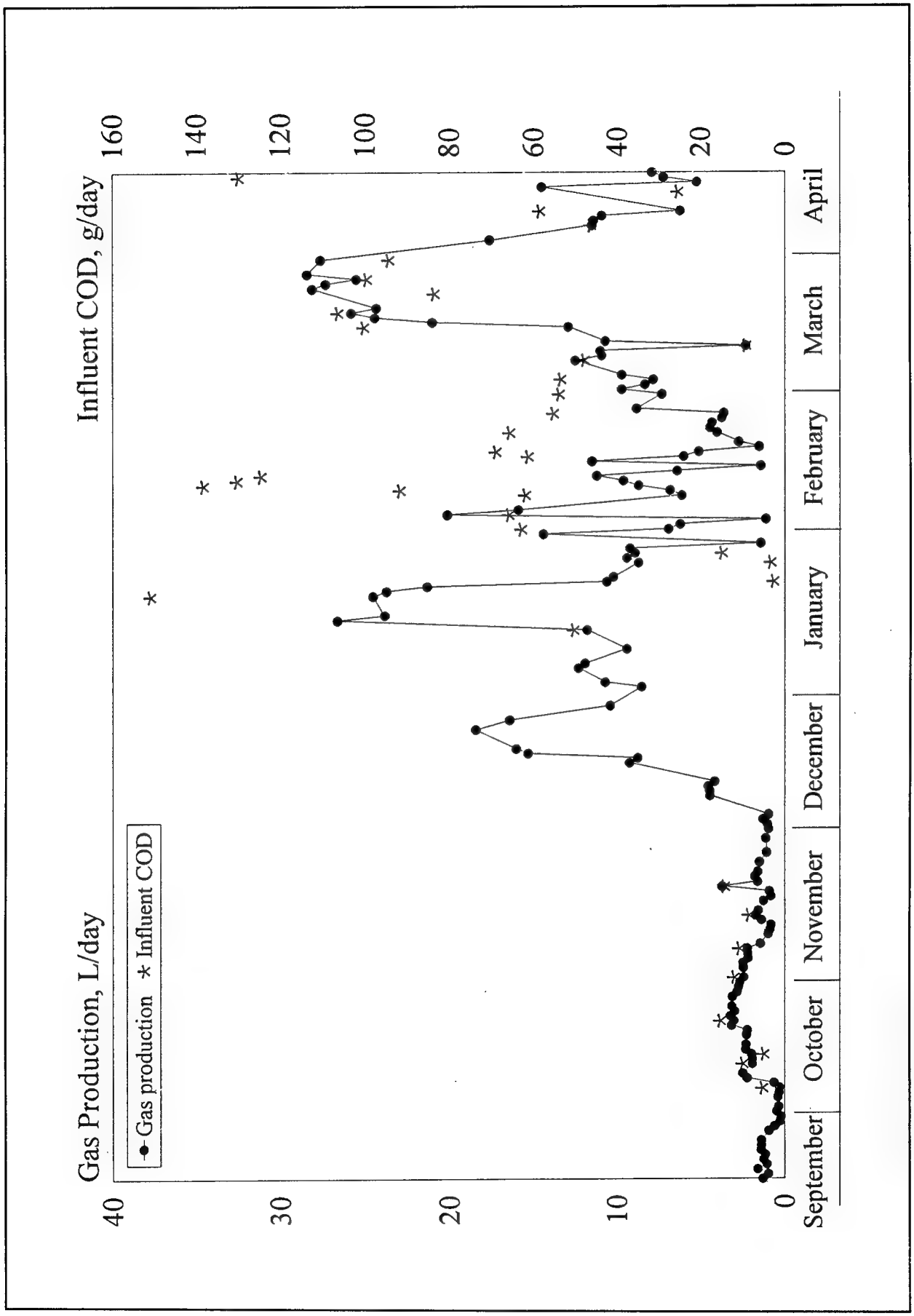

Figure 16. Gas production and influent COD at the field site.

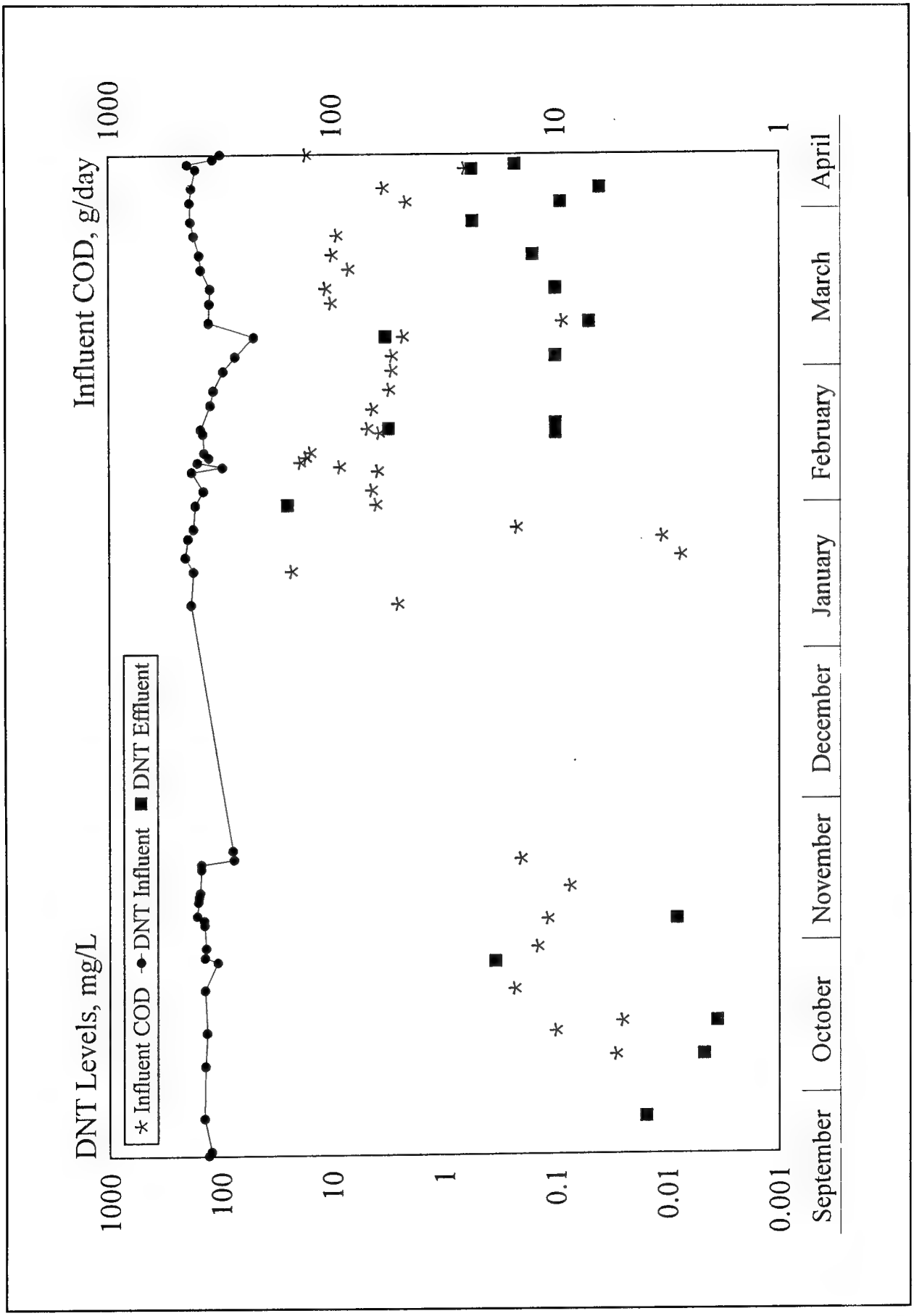

Figure 17. DNT breakthrough compared to influent COD at the field site.

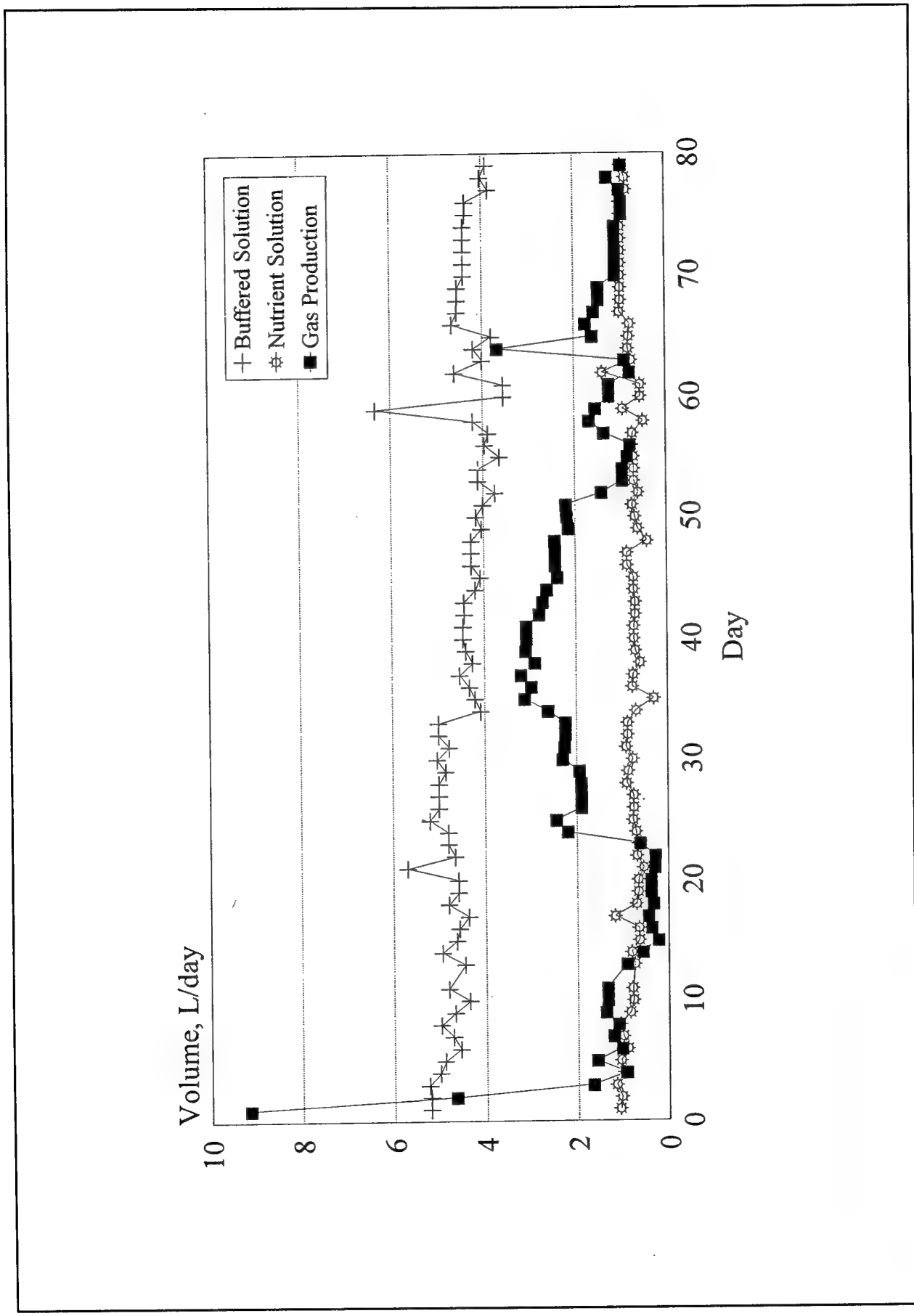

Figure 18. Volume of buffered solution, nutrient solution, and gas production, Phase I.

Table 25. GAC anaerobic analytical data, Phase I.

			Influent, mg/L				Effluent, mg/L									
															Analysis	
Day	Date	Time	DNT	Ether	Alcohol	COD	DNT	Ether	Alcohol	COD	Acetic acid	Propionic acid	Methanol	Ethanol	DNT	DAT
1	9-15-92	14:00	130	400	300	---										
2	9-16-92	13:55	122	20	60	---										
10	9-24-92	10:00	141	150	2650	---				250	ND	ND	ND	ND	0.0154	263.46
14	9-28-92	14:00	---	---	---	---				271	ND	ND	ND	ND	ND	73.52
21	10-5-92	9:30	139	130	2970	---										
23	10-7-92	11:30	---	---	---	1002	0.04			360	ND	ND	ND	ND	0.0047	72.62
28	10-12-92	13:30	134	0	360	1733	ND	ND	ND	360						
30	10-14-92	9:00				875				418	ND	ND			0.0036	87.48
37	10-21-92	14:30	140	50	730	2998	ND	ND	ND	520	ND	ND			ND	95.29
43	10-27-92	8:45	107	0	790		0.35	0	140							
44	10-28-92	8:40	140	170	310						ND	ND			ND	92.87
46	10-30-92	10:00	137	150	80	2510	0	70	0	540						
51	11-4-92	10:00	141	0	660		ND	ND	ND							
52	11-5-92	10:00	142	0	750	2284	ND	90	ND	564	ND	ND			0.0082	107.46
53	11-6-92	9:30	165	0	390		ND	ND	ND							
56	11-9-92	10:00	160	0	320		ND	ND	ND							
57	11-10-92	10:30	158	0	400		ND	ND	ND							
58	11-11-92	11:00	154		60		ND	ND	60							
59	11-12-92	11:00				1832				636	ND	ND			ND	103.25
63	11-16-92	10:00	151				ND									
64	11-17-92	9:30	151	80	790		ND	100	ND							
65	11-18-92	9:00	76	30	457	2858	ND	50	ND	570	ND	ND			ND	92.98
67	11-20-92	10:00	78	36	473		ND	94	ND							

Table 26. Data from CRREL method, Phase I.

Day	Dates	2,6-DAT	2,4-DAT	2-A-4-NT	4-A-2-NT	2,6-DNT	Methanol	Ethanol	Acetic Acid	Propionic Acid
10	09-24-92	*	63.46	0.0556	0.1104	ND	ND	ND	ND	ND
14	09-28-92	*	73.52	0.0388	0.0671	ND	ND	ND	ND	ND
23	10-07-92	*	72.62	0.0583	0.0813	ND	ND	ND	ND	ND
30	10-14-92	*	87.48	0.0556	0.0952	ND			ND	ND
37	10-21-92	*	95.29	0.0464	0.0784	ND			ND	ND
44	10-28-92	*	92.87	0.0086	0.0070	ND			ND	ND
52	11-05-92	*	107.46	ND	0.1892	ND			ND	ND
59	11-12-92	*	103.25	0.0442	0.1653	ND			ND	ND
66	11-19-92	*	92.98	ND	0.1710	ND			ND	ND

Key

* Because the concentration of 2,4-DAT is so high, any 2,6-DAT would be obscured by the leading edge of the 2,4-DAT peak.
ND none detected

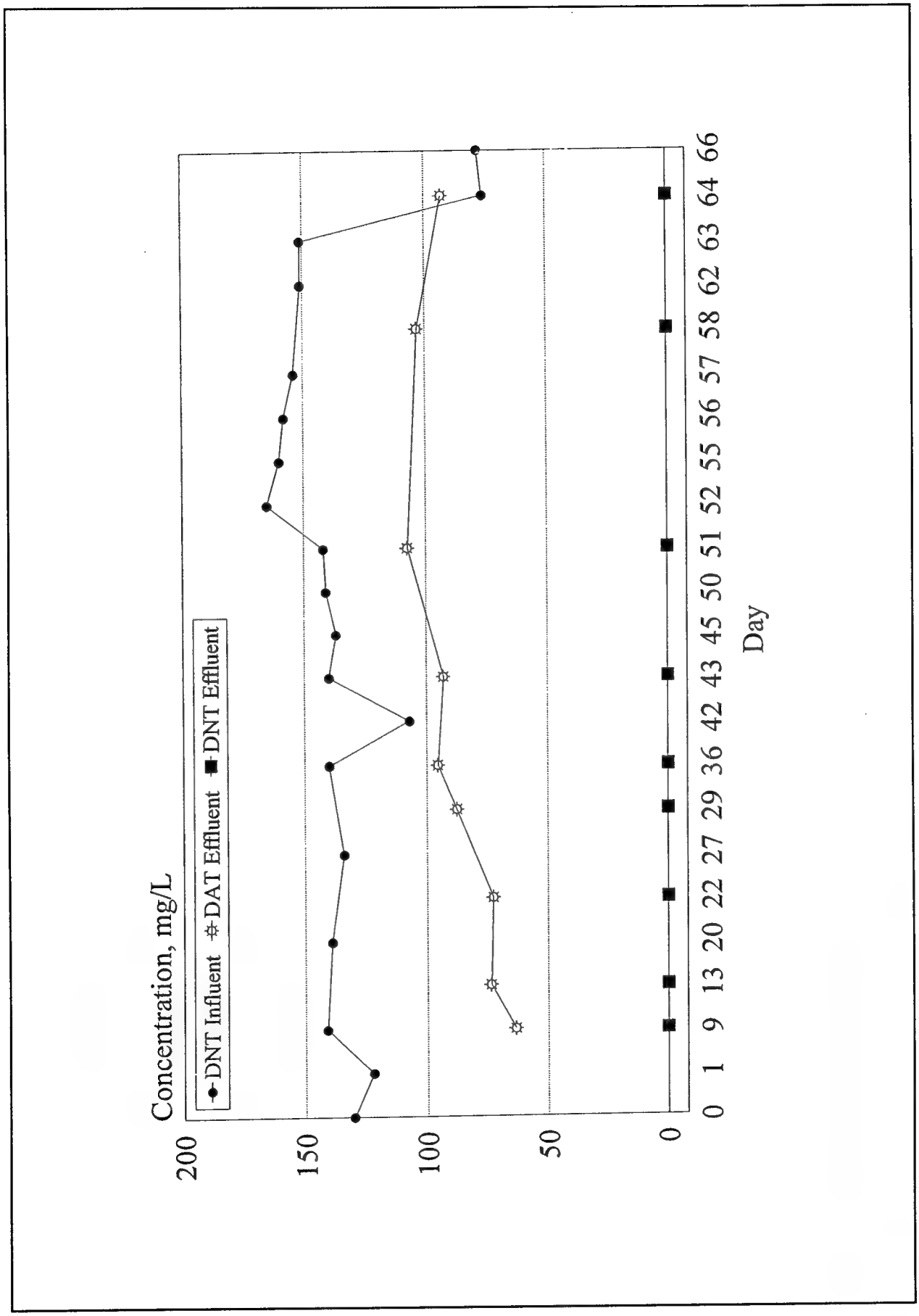

Figure 19. DNT influent, DNT effluent, and DAT effluent, Phase I.

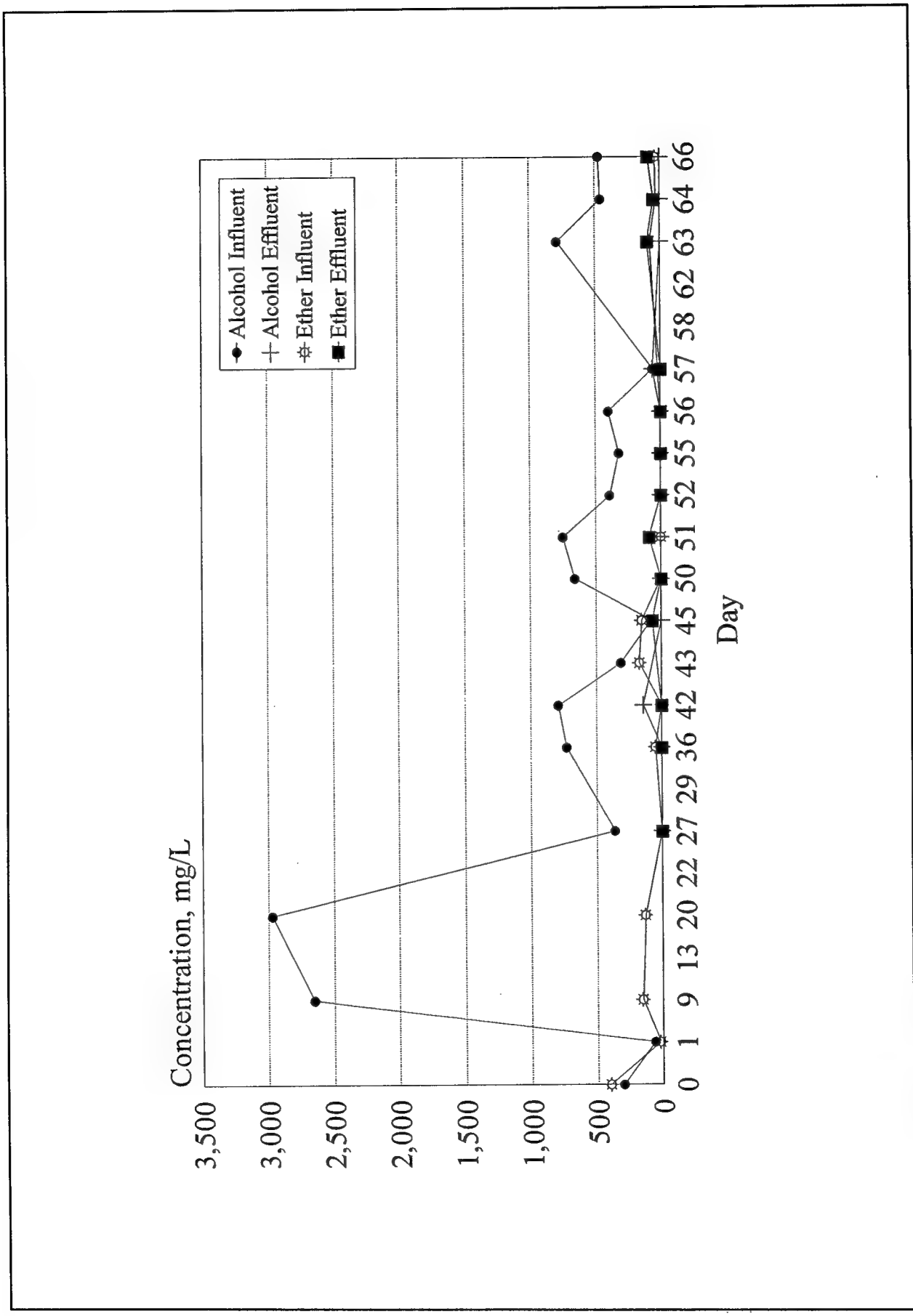

Figure 20. Influent and effluent alcohol and ether, Phase I.

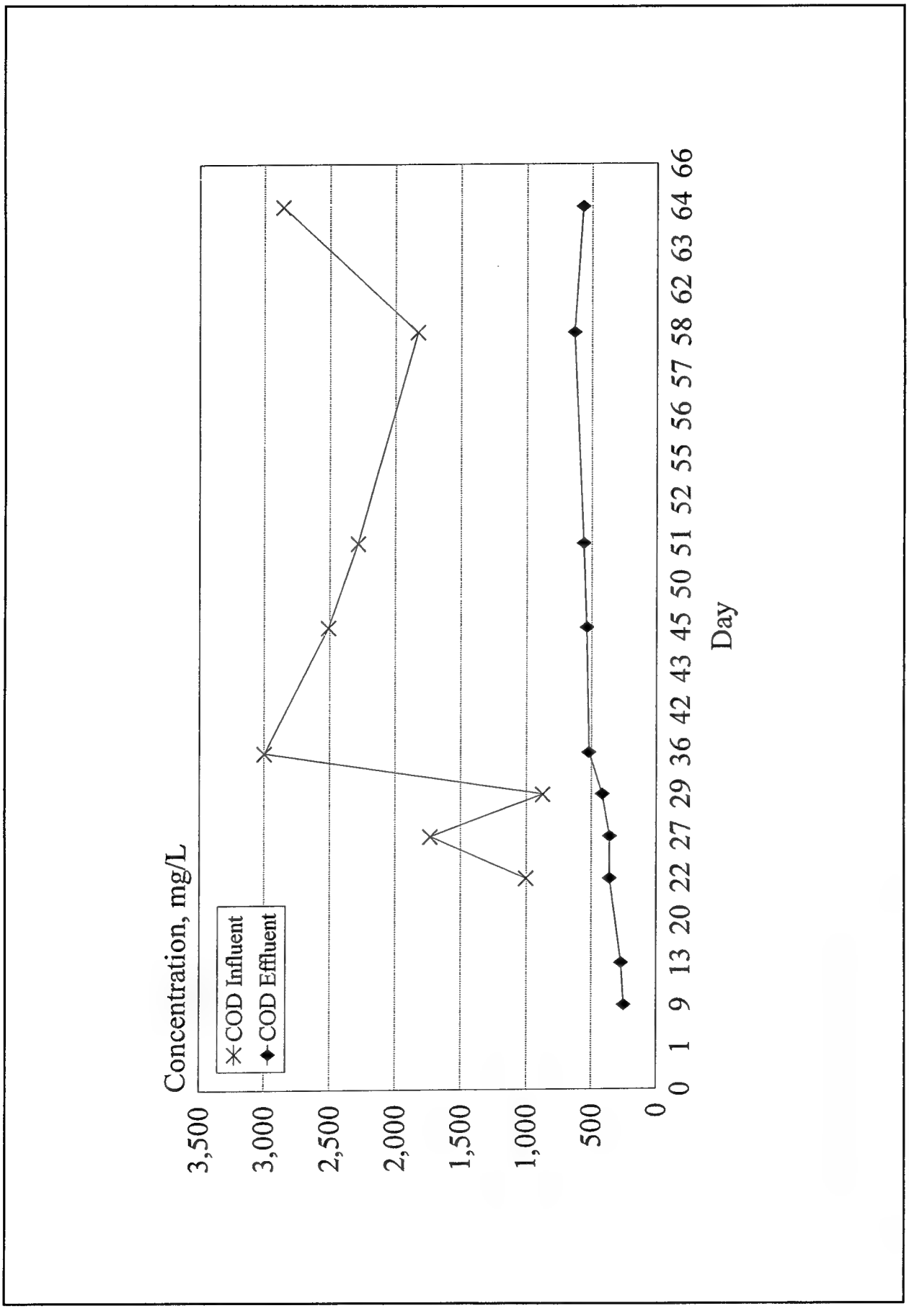

Figure 21. Influent and effluent COD, Phase I.

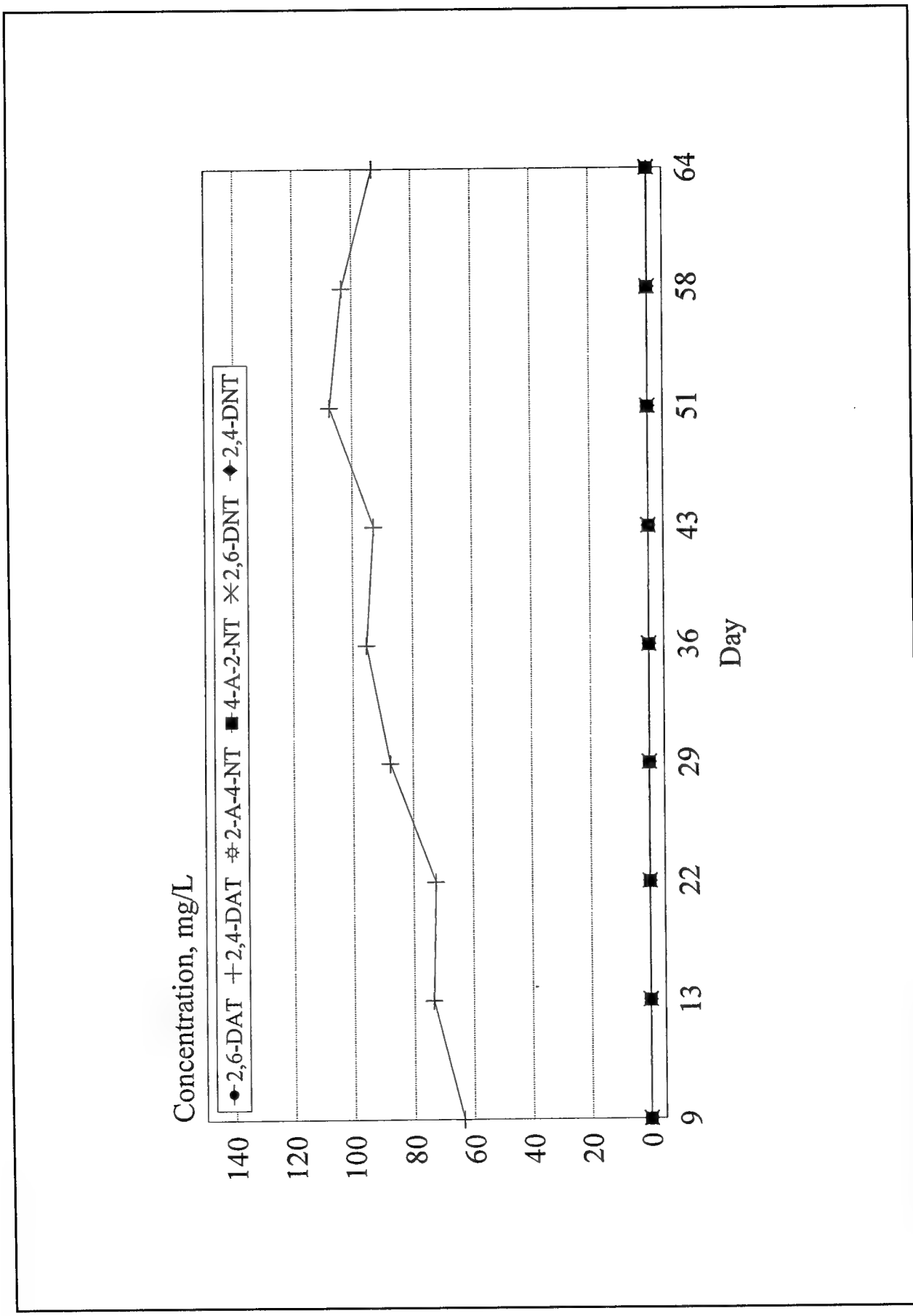

Figure 22. Results from CRREL method of identification of DNT of byproducts, Phase I.

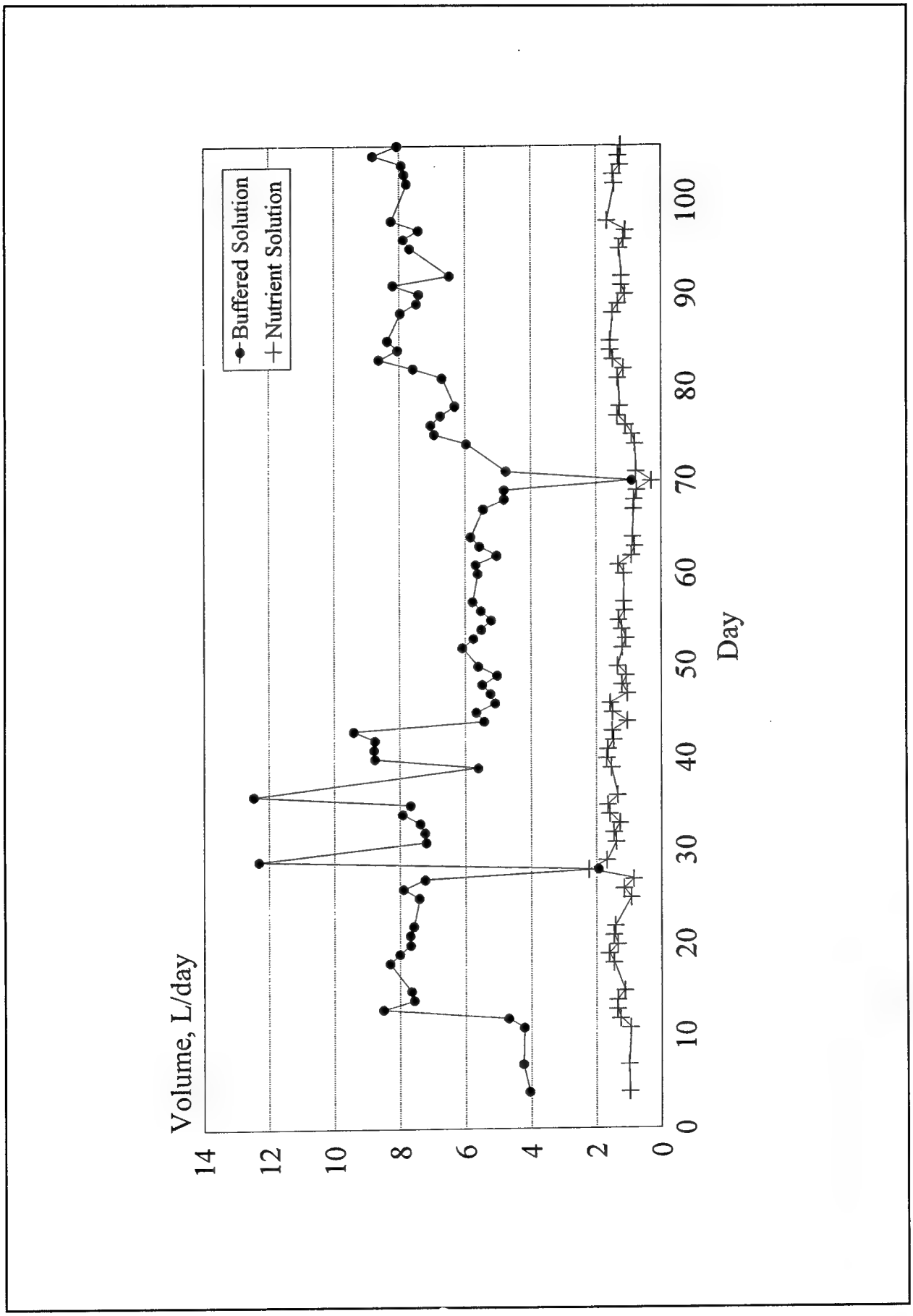

Figure 23. Volume of buffered and nutrient solutions, Phase II.

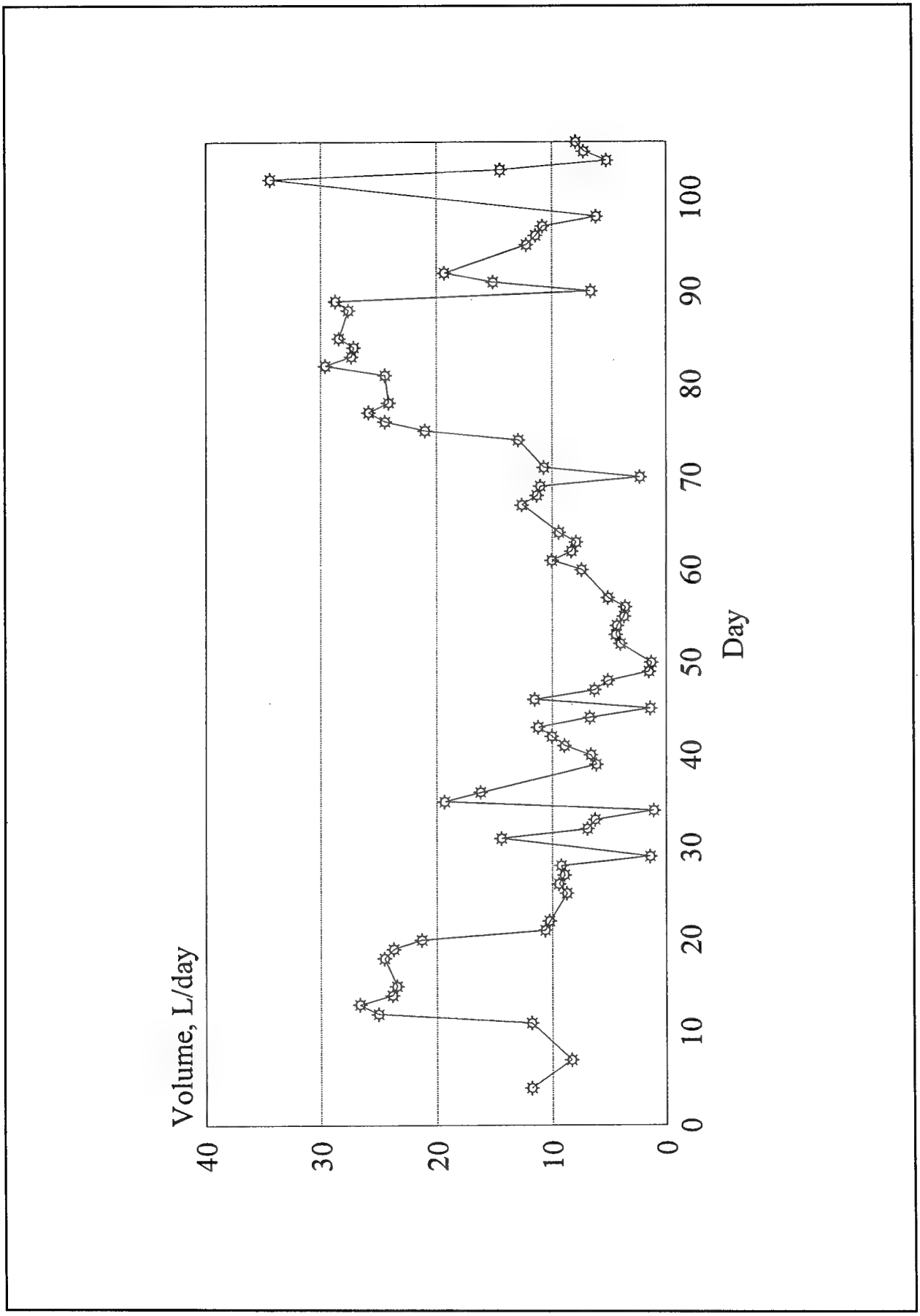

Figure 24. Gas production, Phase II.

Table 27. GAC anaerobic reactor analytical data, Phase II.

			Influent, mg/L				Effluent, mg/L							
Day	Date	Time	DNT	Ether	Alcohol	COD	DNT	Ether	Alcohol	COD	Acetic Acid	Propionic Acid	Methanol	Ethanol
12	01-11-93	10:30 a.m.	184	1287	3256	9800	0	848	0	1000	ND	ND	ND	ND
19	01-18-93	9:00 a.m.	176	558	3377	15550	0	685	0	4500	ND	ND	ND	ND
	01-21-93	2:00 p.m.	208	588	1757	300	0	581	0	0	ND	ND	ND	ND
22	01-25-93	10:00 a.m.	197	423	1510	400	0	510	0	0				
28	01-27-93	2:00 p.m.	176	225	1516	1850	0	457	0	1075	ND	ND	ND	ND
33	02-01-93	11:00 a.m.	169	530	2688	7250	25	533	955	3450	170.1	10.1	ND	909
36	02-04-93	11:00 a.m.	142	614	2856	7080	0	519	0	1325	59.6	3.4	ND	ND
40	02-08-93	10:00 a.m.	182	549	3334	8705	TRACE	649	1237	5970	1982	34.4	ND	1037
41	02-09-93	9:30 a.m.	96	377	3269	8800	0	514	468	5540	3521	79	ND	462
42	02-10-93	9:30 a.m.	161	352	4801	13300	0	493	64	4915	3276	69.1	ND	68
43	02-11-93	7:30 a.m.	126.5	282	3766	12750	0	541	112	5650	3460	42.2	ND	113
44	02-12-93	8:00 a.m.	140	1093	4387	11438	0	736	123	5870	3634	29	ND	115
48	02-16-93	2:00 p.m.	143	150	4152	9800	0.1	52.2	5.4	350	127	TRACE	ND	5
49	02-17-93	10:00 a.m.	150	1248	3808	10350	3.1	273	1123	3895	343	1.9	ND	959
54	02-22-93	3:00 p.m.	123	384	3386	9063	0.1	328	754	5120	2137	2.8	ND	765
57	02-25-93	9:00 a.m.	115	362	3086	8338	0	310	801	4920	2039	2.3	ND	825
61	03-01-93	9:30 a.m.	94	472	2806	7800	0	294	3.4	3010	1531	8.6	ND	3.8
64	03-04-93	9:30 a.m.	73	551	2975	8413	0.1	443	1.5	2945	1841	9	ND	1.3
68	03-08-93	9:00 a.m.	49.6	67	2989	7638	3.3	299	TRACE	1125	210	4.2	ND	ND
71	03-11-93	1:45 p.m.	127.4	600	2875	7813	0.05	300	0	950	113	TRACE	ND	ND
75	03-15-93	9:00 a.m.	125.4	512	4675	14863	0	294	1.9	1055	33.8	ND	ND	4
78	03-18-93	9:00 a.m.	123.3	808	4657	13200	0.1	505	2.1	1215	54.5	ND	ND	5

Table 27. (Cont'd).

			Influent, mg/L				Effluent, mg/L							
Day	Date	Time	DNT	Ether	Alcohol	COD	DNT	Ether	Alcohol	COD	Acetic Acid	Propionic Acid	Methanol	Ethanol
82	03-22-93	9:00 a.m.	148.9	377	4103	10738	0	452	3.8	1195	27.1	ND	ND	2.6
85	03-25-93		154.3	304	3843	10050	0.16	355	TRACE	870	21.1	2.3	ND	TRACE
89	03-29-93		173.2	264	3839	10000	ND	323	4.4	803	17.2	43.9	ND	2.6
92	04-01-93	10:00 a.m.	184	421	2819	7625	0.55	331	13.9	3273	1641	65.6	ND	11.9
95	04-05-93	8:30 a.m.	187	236	1922	5113	0.09	254	3.2	970	12.6	132	ND	0.5
98	04-08-93	10:00 a.m.	182	172	896	5863	0.04	181	ND	913	4.3	13.9	ND	ND
102	04-12-93	10:00 a.m.	166	2058	9212	27725	0.56	396	3.5	1524	20.3	225	ND	3.5
103	04-13-93*		196	1458	9215		0.23	806	3594					
103	04-13-93		116	863	4878									
105	04-15-93	10:00 a.m.	100	645	4722	12863	ND	653	2060	10063	2500	TRACE	ND	1900

* After dilution.

Table 28. Byproduct analysis, Phase II.

Day	Date	2,6-DAT	2,4-DAT	2-A-4-NT	4-A-2-NT	2,6-DNT	2,4-DNT
12	1-11-93		205			0.05**	
19	1-18-93		141				
22	1-21-93		108				
40	2-8-93	6.3	66.0	0.42	0.89	ND	1.16**
41	2-9-93	6.9	37.9	0.39	0.48	ND	ND
42	2-10-93	5.2	26.9	0.11	0.62	ND	ND
43	2-11-93	ND*	26.9	0.04	0.07	ND	ND
44	2-12-93	1.8	26.6	0.05	0.08	ND	ND
82	3-22-93	ND*	47.6	0.09	0.22	ND	0.13
85	3-25-93	ND*	51.1	0.05	0.12	ND	0.03
89	3-29-93	ND*	53.3	ND	0.04	ND	ND
92	4-1-93	ND*	40.3	0.01	0.04	ND	ND
93	4-2-93		55.7				
95	4-5-93	ND*	60.6	ND	0.05	ND	ND
98	4-8-93	ND*	65.1	ND	ND	ND	ND
102	4-12-93	ND*	103.9	ND	0.40	ND	ND
105	4-15-93	ND*	13.1	0.07	0.11	ND	ND

* Because the concentration of 2,4-DAT is so high, any 2,6-DAT would be obscured by the leading edge of the 2,4-DAT peak.
** Questionable.
ND None detected.

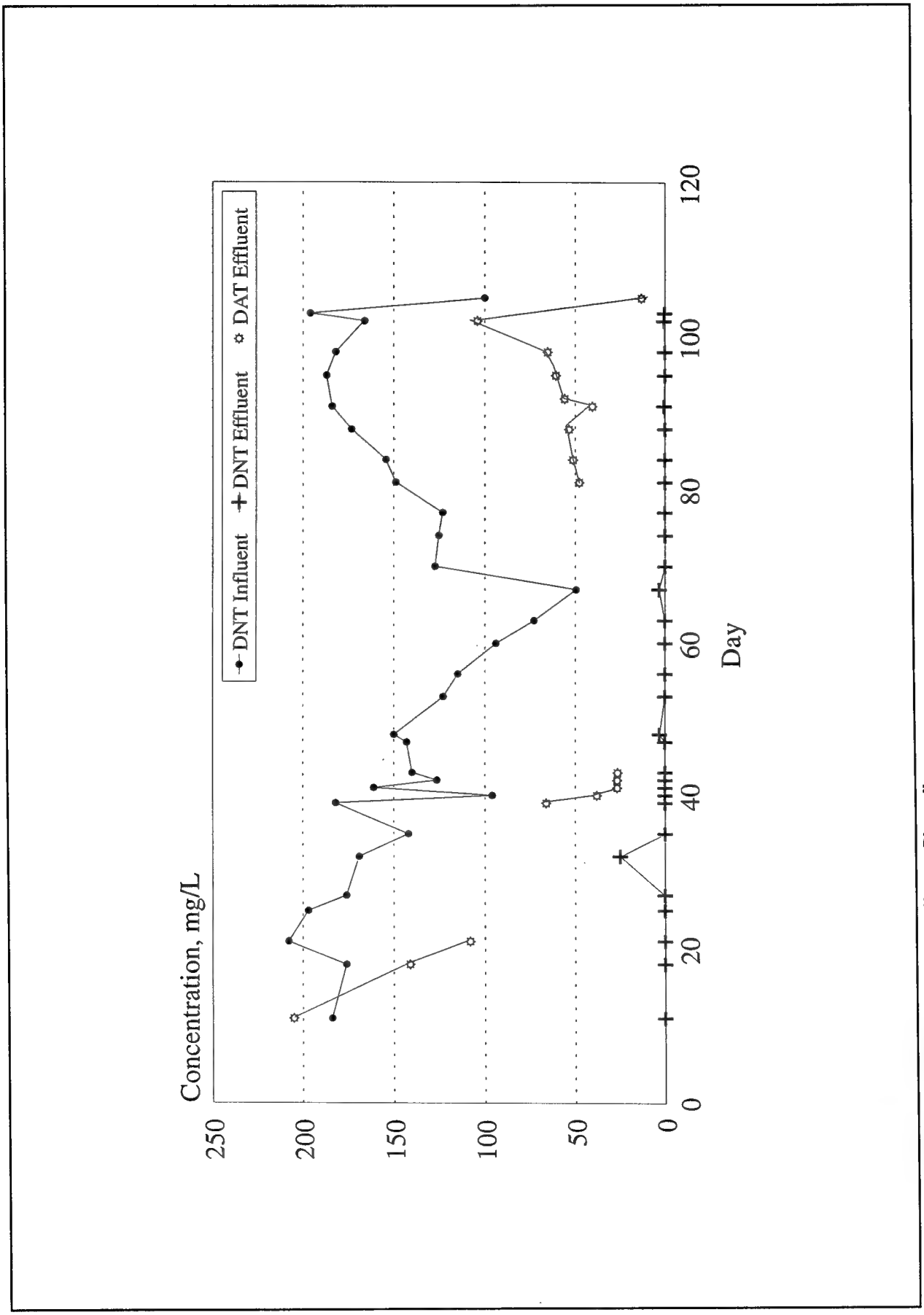

Figure 25. DNT influent, DNT effluent, and DAT effluent, Phase II.

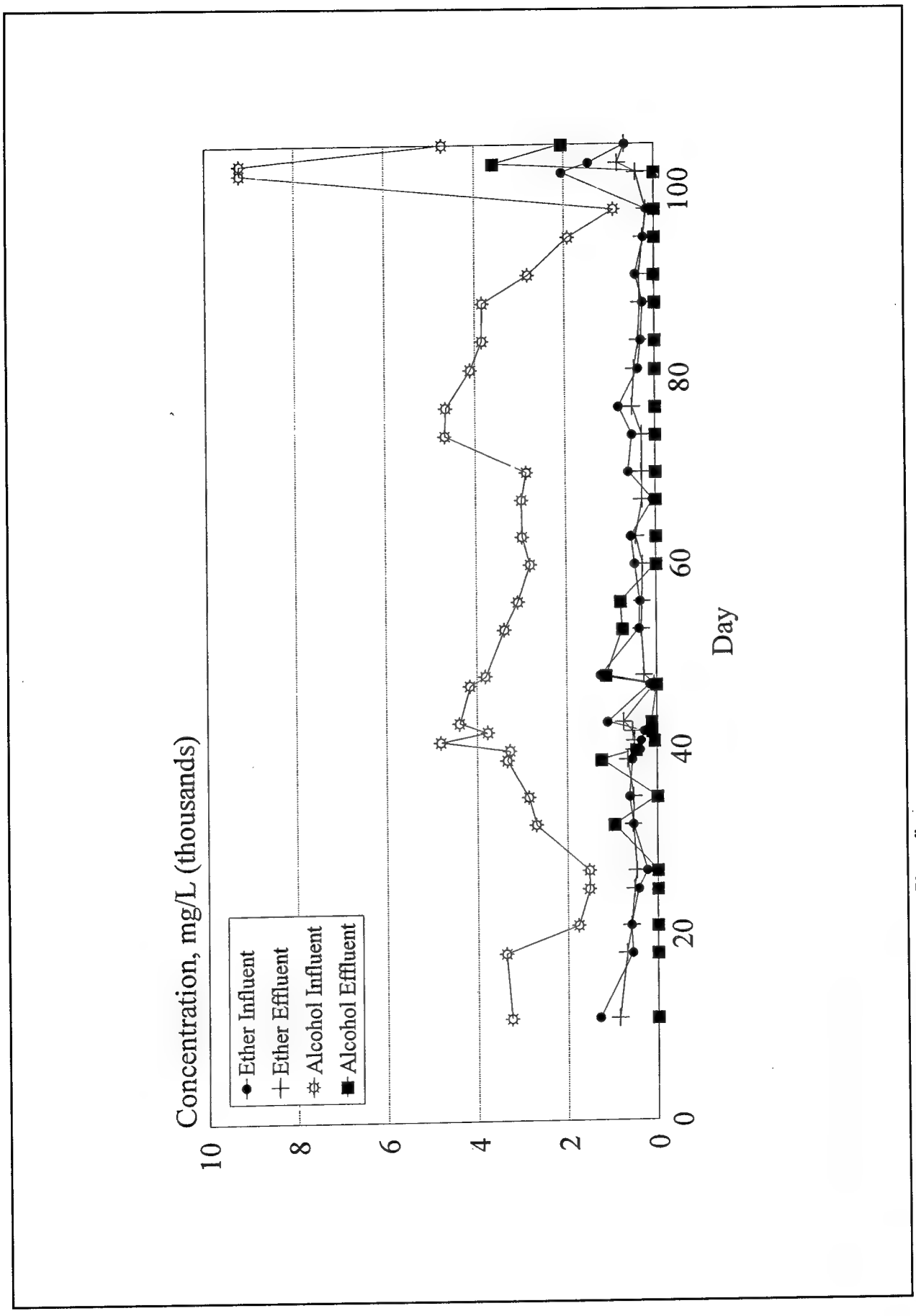

Figure 26. Influent and effluent alcohol and ether, Phase II.

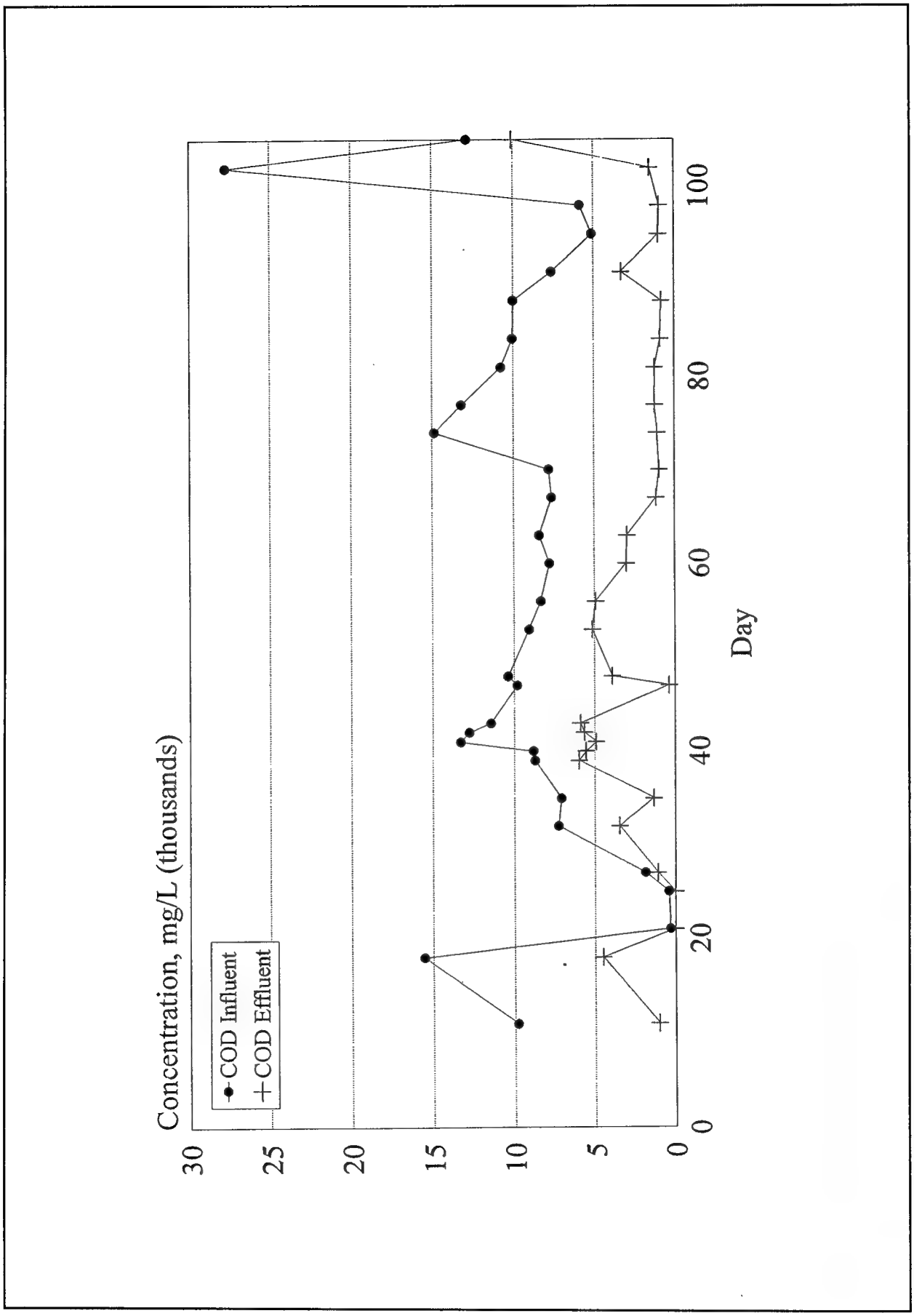

Figure 27. Influent and effluent COD, Phase II.

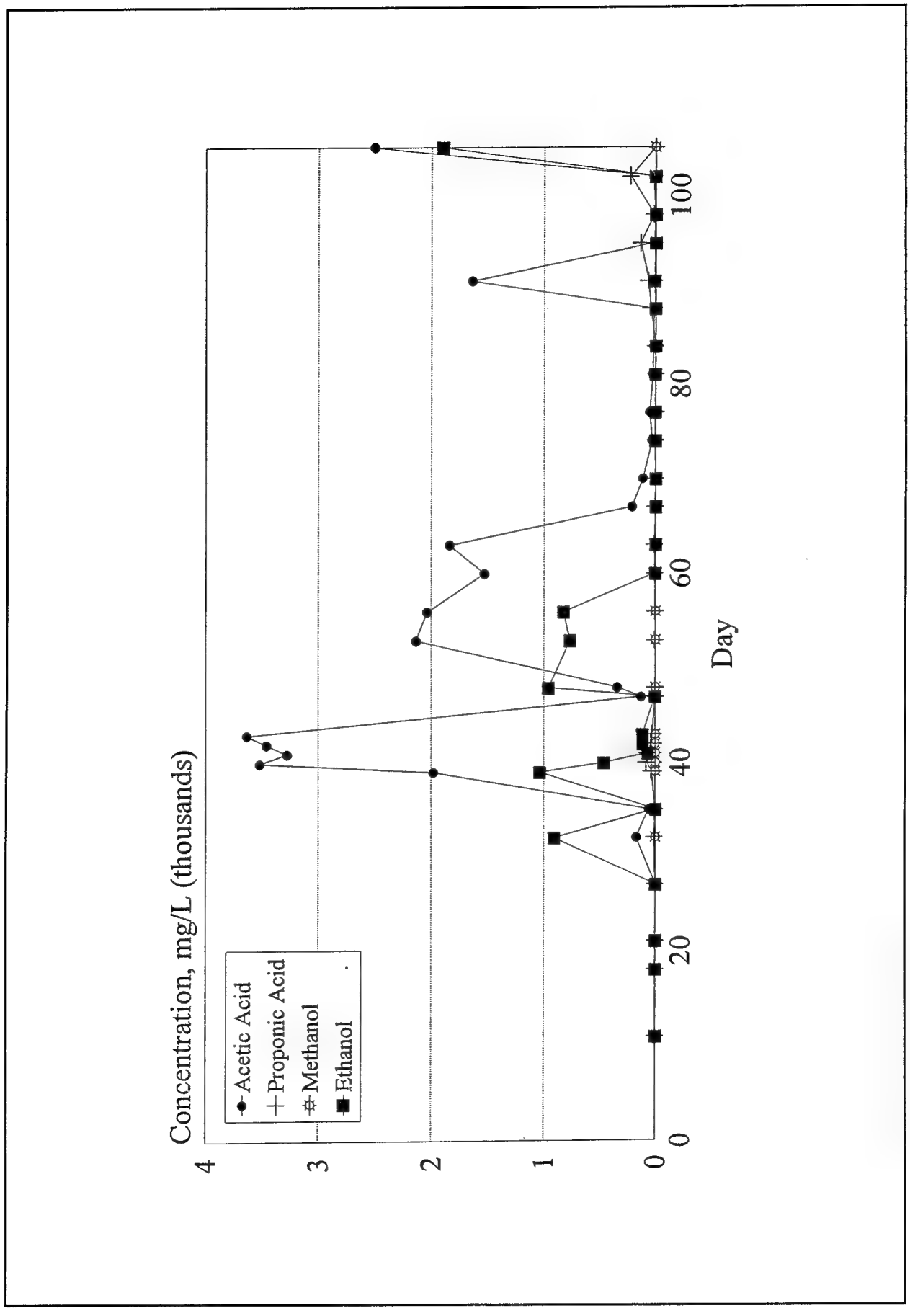

Figure 28. Fatty acids/alcohol analysis, Phase II.

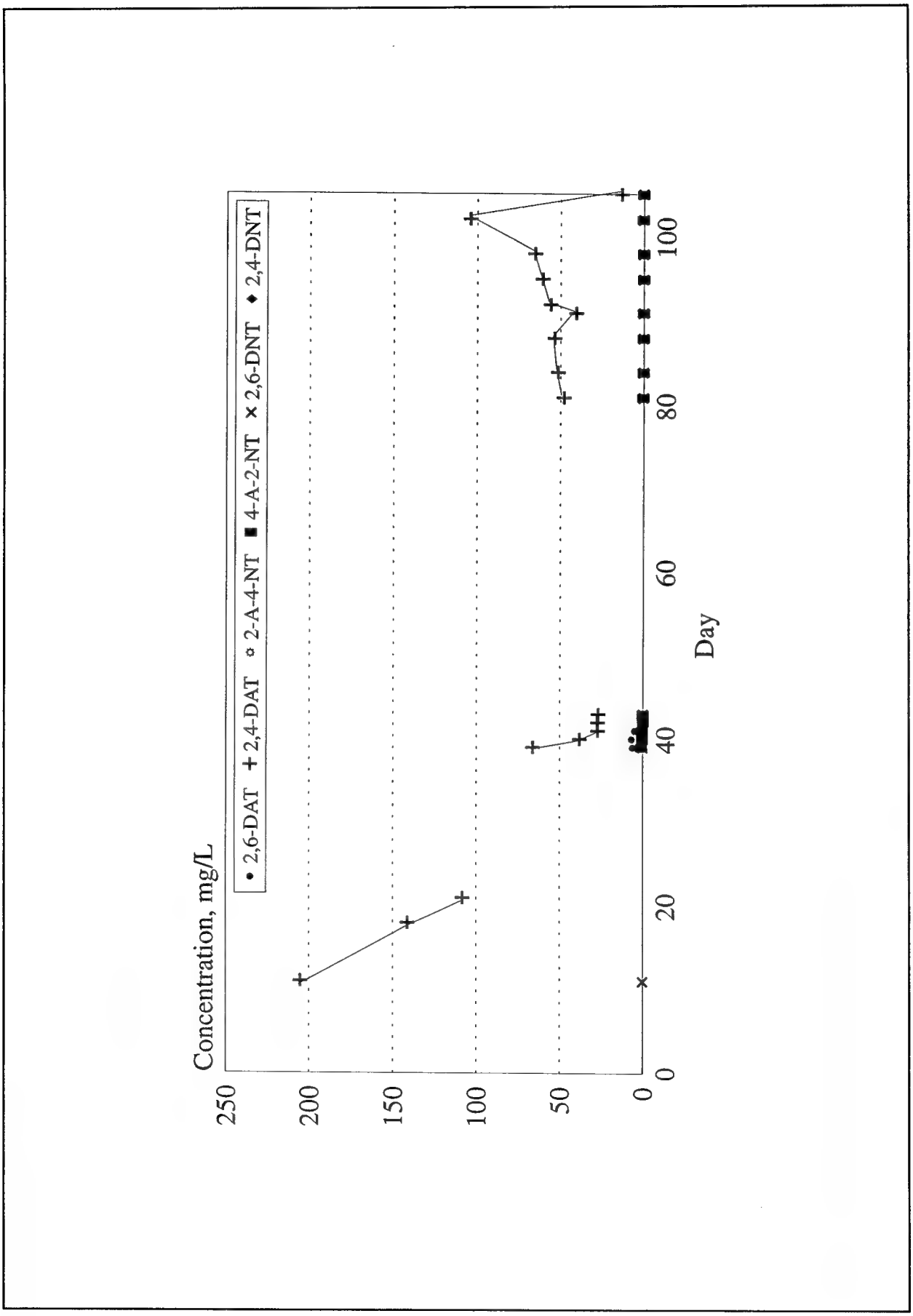

Figure 29. Results from CRREL method for identification of DNT and byproducts, Phase II.

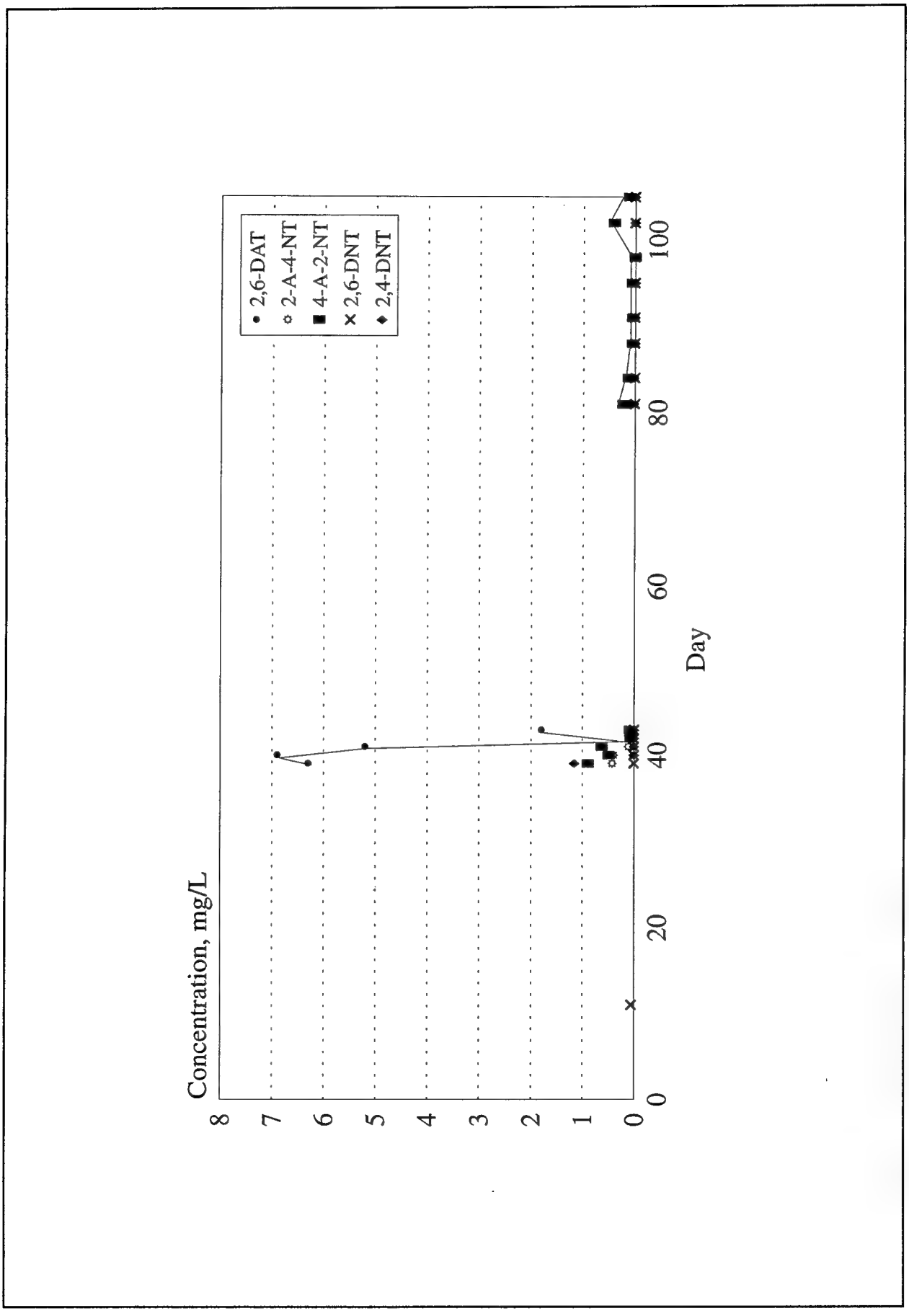

Figure 30. Results from CRREL method for identification of DNT and byproducts excluding DAT, Phase II.

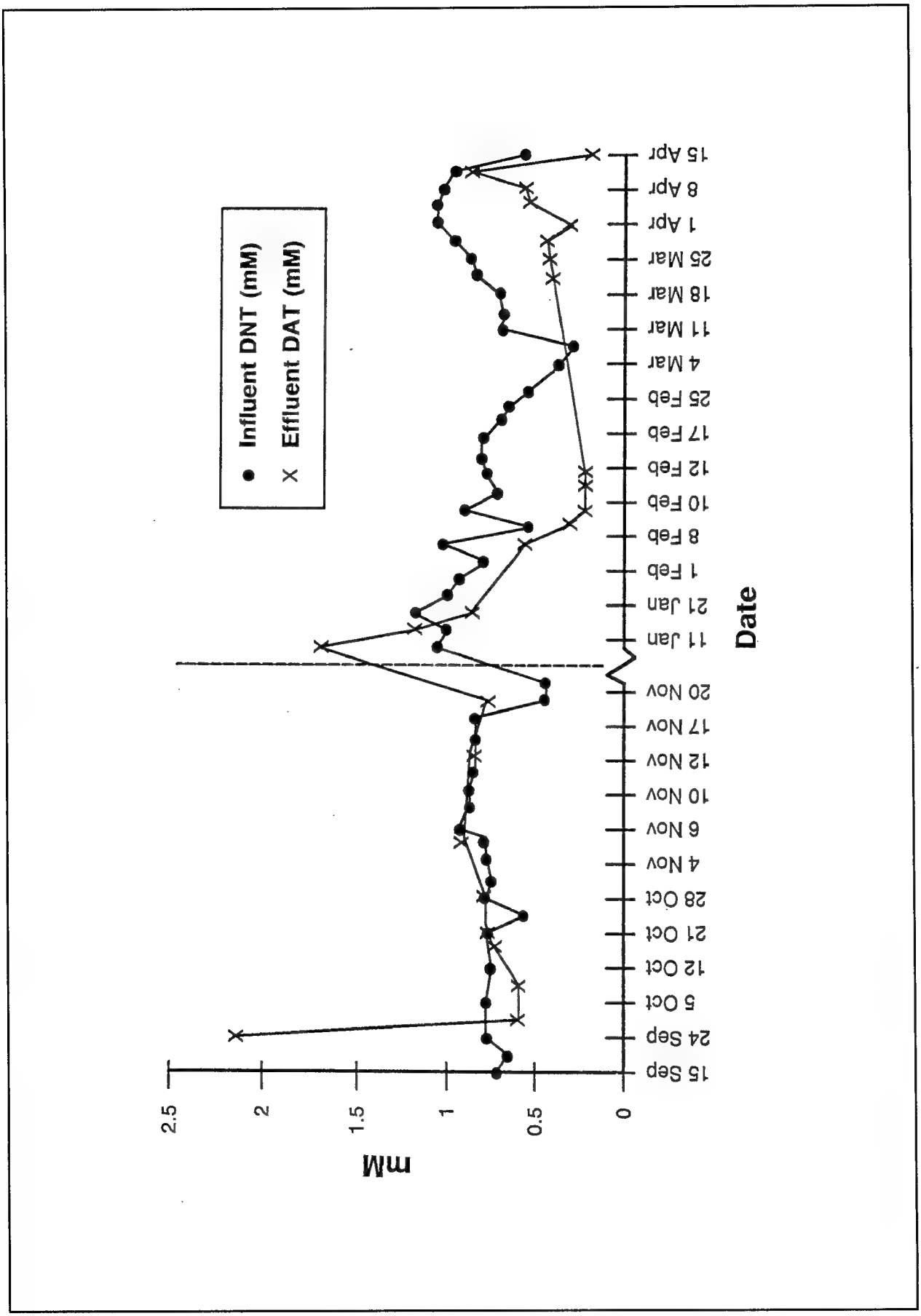

Figure 31. Molar balance on DNT/DAT species.

Table 29. Operating flow rates during the field study.

Operating Period	Month	Day	Flow, L/day
Constant Flow	Sept. - Nov.	1-67	6
Idle (No Analysis)	Dec. - mid Jan.	68-117	5
Increaseing Rates	mid Jan. - mid April	118-149	9.8
		150-189	6.7
		183-201	8.1
		202-213	9

5 Conclusions and Recommendations

Conclusions

Anaerobic fluidized-bed GAC bioreactors efficiently reduced the COD of propellant production wastewater while at the same time reducing DNT to DAT. When ethanol was removed from the feed, however, the bioreactors began failing to biotransform DNT, and the DNT concentration in the bioreactor effluent consequently increased. The principal transformation product of DNT was DAT. Bioreactors under stable conditions showed essentially one-to-one conversion of the DNT on a molar basis. Two second-stage activated sludge reactors successfully degraded the DAT to below detectable limits.

The treatment scheme of an anaerobic bioreactor followed by a second-stage activated sludge process is highly effective in treating DNT and its intermediate products, as long as sufficient ethanol is fed into the anaerobic process. Of the concentrations evaluated in this study, 200 mg/L of ethanol was determined to be the minimum concentration needed to effect the reduction of DNT to DAT.

The use of anaerobic treatment in a fluidized-bed bioreactor containing GAC as the microbial support, followed by aerobic wastewater treatment, has been shown feasible in a controlled laboratory environment. The anaerobic GAC reactor has also demonstrated effectiveness on high-strength wastewater under field conditions, but the subsequent aerobic process has not been tested in the field.

Recommendations

Automated control of pH and bed height should be incorporated in scalable demonstrations of this technology. The results of the field test of the bench scale reactor are insufficient to judge the economic viability or operability of this process.

Sequential application of the anaerobic GAC bioreactor and an aerobic wastewater unit operation should be tested on actual wastewater under field conditions, to determine whether the aerobic process will provide mineralization of DAT in these conditions.

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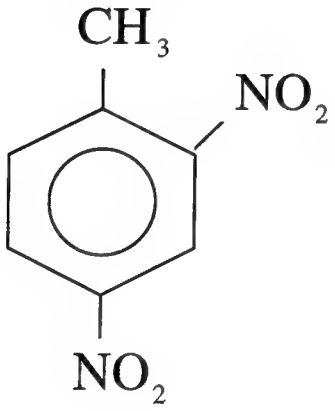
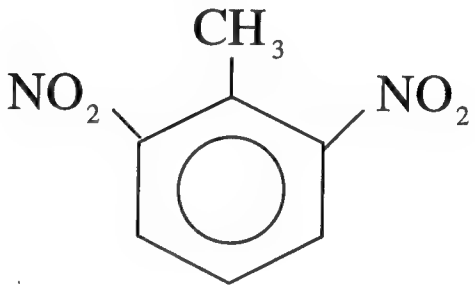
Appendix A: Abbreviations and Structure of DNT, DAT, and A - NT

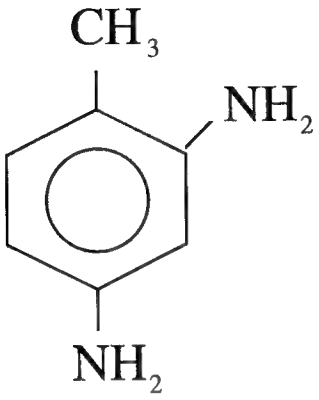
The two structural isomers of DNT that are of main concern are 2,4-DNT and 2,6-DNT. Since 95% of the total DNT found in the water-dry operation is 2,4-DNT, "DNT" will represent 2,4-DNT; if there is a reference to 2,6-DNT, that will be explicitly stated in the text. Likewise, "DAT" will refer to 2,4-DAT (2,4-diaminotoluene), which is also the major isomer found in these experiments (there are also two isomers for DAT, 2,4-DAT and 2,6-DAT). The other biotransformed products that are formed in the DNT biodegradation process are 2-A-4-NT (2-amino-4-nitrotoluene) and 4-A-2-NT (4-amino-2-nitrotoluene). Following is a schematic of these six compounds.



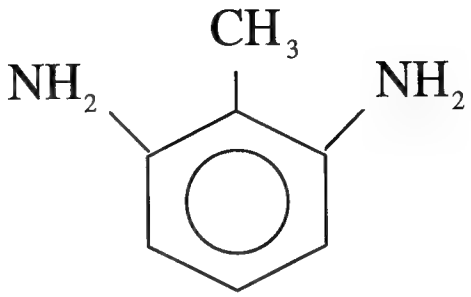
2,4-Dinitrotoluene (DNT)



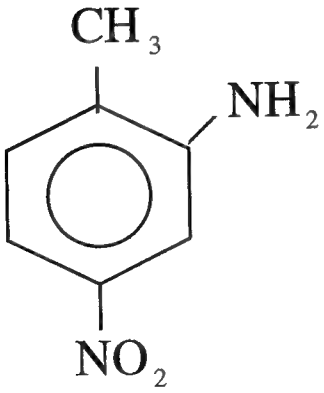
2,6-Dinitrotoluene (2,6-DNT)



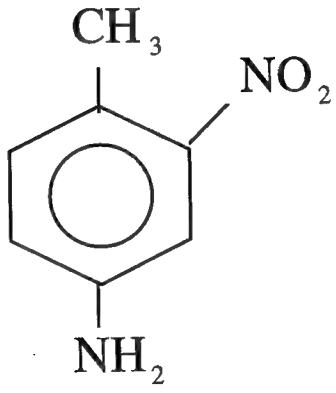
2,4-Diaminotoluene (DAT)



2,6-Diaminotoluene (2,6-DAT)



2-Amino-4-Nitrotoluene (2-A-4-NT)



4-Amino-2-Nitrotoluene (4-A-2-NT)

Appendix B: Toxicity of DAT

The presence of DAT in the effluent stream is important because it is a suspected cancer-causing agent. There are currently no toxicity levels because insufficient data on DAT exposure in humans is available for carcinogenic evaluation, although there is enough data to support carcinogenic activity in laboratory animals. DAT causes a variety of abnormalities including sarcomas and carcinomas in both male and female rats and female mice (male mice did not show notable tumor increases), as well as causing chronic liver damage. By comparison, benzene, a known human carcinogen, attacks genetic material as well as the blood supply, whereas DNT (and 2,6-DNT) primarily invades the reproductive system (in both males and females) (Sigma Aldrich, p 1059; U.S. Department of Health and Human Services).

DAT is usually found as an intermediary in toluene diisocyanate production (which in turn is used to manufacture polyurethane). It is also used, in small amounts, in certain dye formulas, such as those used for coloring silks, leathers, furs, wool and some biological stains. Prior to 1971, DAT was used in certain hair-dye formulas. (It appears that even though these hair dyes were widely used, DAT was not present in significant enough quantities to provide a great carcinogenic risk.) There is concern that trace amounts of DAT left in the dyes can be passed on to the community at large (U.S. Department of Health and Human Services 1991, p 147; Searle and Teal 1990, p 112).

DAT can be introduced into the body through inhalation, ingestion, or absorption, all of which cause detrimental effects to animals. Skin absorption is the primary method of exposure, with inhalation being far less common and direct ingestion being used in laboratory analysis only. Absorption leads to methemoglobin production, which, in large enough quantities, leads to cyanosis (blueness of skin resulting from oxygen deficiency), although the concentration required for the beginning of methemoglobin production is not known. Other dangers surrounding DAT involve its solubility in specific solvents. It is very soluble in hot water, ethanol, ether, and hot benzene. During thermal decomposition, it releases toxic fumes composed of carbon monoxide, carbon dioxide and nitrogen oxides. Due to its high solubility in water, industrial wastewaters (in the toluene diisocyanate production process) are considered the main route through which contamination could take place. Air emissions during this production process are thought to be at concentrations unable to significantly affect the general population (Sigma Aldrich, p 1059; U.S. Department of Health and Human Services 1991, pp 147, 148).

The most current toxicological information on DAT shows that International Agency for Research on Cancer (IARC) put this compound in the 2B group, which is defined by "the working group concluded that the listed agents are possibly carcinogenic to humans." (IARC has five groups total: 1, 2A, 2B, 3 and 4, with definitions ranging from "the listed agents are carcinogenic to humans" [1] to "the listed agent is probably not carcinogenic to humans" [4].) National Institute for Occupational Safety and

Health (NIOSH) standards indicate the tumorigenic data defines it carcinogenic (to animals). All listed information points to this substance as probably being carcinogenic in humans although the levels at which it begins to harm are unknown (Sweet 1992).

A ranking of various aromatic amines and nitro compounds was created, including DAT and DNT, based on (1) the weight of evidence against the compound as a cancer causing agent and (2) a potency indicator (namely, the TD_{50} value, which is defined as the chronic dose rate [in mg/kg body weight per day] which would create a toxicity response in 50% of the defined population of experimental animals). The ranking categories range from Proven Human (carcinogen) through Classes A, B, C, and D (A being more "hazardous" than D) and Incapable of Classification to Negative Evidence. Using this system of classifying possible carcinogenic compounds, DAT is ranked first in Class A (proven carcinogenic activity in animals and corresponding TD_{50} value) whereas DNT is ranked in the middle of Class C (mixture of suspected and proven carcinogenic activity in animals and a corresponding TD_{50} value). Interestingly, 2,6-DAT is ranked in the category of Negative Evidence while 2,5-DAT is listed in the category of Incapable of Classification (due to inadequate studies and no clear evidence of animal carcinogenicity). This method of classification is a combination of qualitative and quantitative information about 38 selected compounds and was written as a guide to nontoxicologists in developing workplace hygiene controls (Crabtree *et al.* 1991).

Appendix C: Hazards Analysis Evaluation

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and
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March 31, 1993

HI-93-M-014
Hazards Analysis of Bench-Scale Granular Activated Carbon
Anaerobic Reactors for Treatment of DNT Wastewater - ME-117

Objective

The objective of this study is to perform a Hazards assessment of the bench-scale Granular Activated Carbon (GAC) reactor installed in Building 5511.

The GAC is used to treat wastewater containing ppm quantities of DNT.

Summary and Conclusion

It is concluded from this Operating Hazards Analysis (onsite process equipment and procedure review) that the GAC and established operating procedure[1] are acceptably safe for treating wastewater from the water dry operations containing ≤184 ppm DNT. No initiation hazard is present at this concentration and the DNT residue is not allowed to become dry.

Small quantities of off-gas from the reactor (6 liters/day, 90% methane) are piped outside the building, so no flammable gas accumulation hazard results. Wastewater, nutrient and buffer solutions in laboratory or bench-scale quantities are handled per established procedures and safety practices.

This analysis applies only to the bench-scale GAC anaerobic reactor. Should a larger-scale unit be installed, further hazards assessment may be needed to assure adequate safety to personnel and facility.

HI-93-M-014 March 31, 1993

Future Work

No further effort is planned.

Recommendations

No recommendations are made as a result of this study.

INTRODUCTION

The bench-scale GAC anaerobic reactor is being evaluated for removal and destruction of PPM concentrations of DNT in wastewater. This technology was developed by Civil and Environmental Research Laboratory (CERL) and the University of Cincinnati with artificial DNT in wastewater. The reactor is being evaluated at RAAP with DNT containing wastewater.

A flow diagram of the FAC anaerobic bioreactor is shown in Figure 1. Basically, the biomass is contained on the granular activated carbon in the reactor column. DNT in the wastewater feed is absorbed by the activated carbon where it can be destroyed by the biomass. Flow through the column is maintained at a rate sufficient to fluidize the FAC bed/biomass but not high enough to cause solids to flow out the top of the column with the effluent. Buffer and vitamin solutions are maintained at the proper conditions for a healthy biomass. Gases and liquid effluent are periodically sampled to evaluate the reactor operation

This OHA was conducted by on-site inspections, procedure review, and discussions with Engineering personnel.

DISCUSSION

It is concluded from the review and observations that the procedural instructions are adequate and the operation is acceptably safe.

Some concern was expressed over potential health hazards to personnel from exposure to biomass microbes. An inquiry[2] resulted in the information that the biomass consists of normal sewage treatment microorganisms and should result in no health hazard to personnel with proper precautions.

HI-93-M-014 March 31, 1993

REFERENCES

[1]Operating procedure 4-26-111, Rev. 0, Evaluation of Wastewater containing 2, 4-DNT.

[2]Letter to James G. Heffinger, Hercules Incorporated, from Sandra Berchtold, University of Cincinnati, dated August 28, 1992. Re: Telephone conversation on the possible hazardous effects of the microbial cultures used in the GAC reactor.

WA6:nns
HI-93-M-014

Abbreviations

2-A-4-NT	2-Amino-4-Nitrotoluene
4-A-2-NT	4-Amino-2-Nitrotoluene
AEC	Army Environmental Center
COD	Chemical Oxygen Demand
CRREL	Cold Regions Research Engineering Laboratory
DNT	Dinitrotoluene
DAT	Diaminotoluene
EPA	Environmental Protection Agency
GAC	Granular Activated Carbon
GC	Gas Chromatograph
GC/MS	Gas Chromatograph/Mass Spectroscopy
GOCO	Government Owned, Contractor Operated
Hercules	Hercules Aerospace Company
HML/HWRIC	Hazardous Material Laboratory/Hazardous Waste Research and Information Center
HPLC	High Performance Liquid Chromatography
IARC	International Agency for Research on Cancer
mM	millimolar
M	molar
N	normal
ND	Not Detected
NIOSH	National Institute for Occupational Safety and Health
NPDES	National Pollution Discharge Elimination System
RAAP	Radford Army Ammunition Plant
TNT	Trinitrotoluene
USACERL	U.S. Army Construction Engineering Research Laboratories

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